Are pyrethroid insecticides a threat to aquatic non-target species?

Michael J. Lydy

SIU Southern Illinois University
CARBONDALE

Presented at U of I – 3 March 2017

Acknowledgements

Collaborators:
Don Weston, Erin Amweg, Robert Gilliom, Jeff Martin, Robert Holmes, Scott Ogle, Minghua Zhang, Cathy Johnson, Helen Poynton, Gary Wellborn, Lisa Hunt

Students and Post-docs:
Troy Anderson, Jason Belden, Amanda Brennan, YuPing Ding, Amanda Harwood, Emily Hintzen, Huizhen Li, Tyler Mehler, Jon Maul, Charlene Ng, Sari Pehkonen, Andrew Trimble, Jing You, Yuanbo Li, Jennifer Heim, Kaley Major

Technicians and researchers:
Rebecca Kelley, Amanda Brennan, Trish Trimble, Kara Huff Hartz

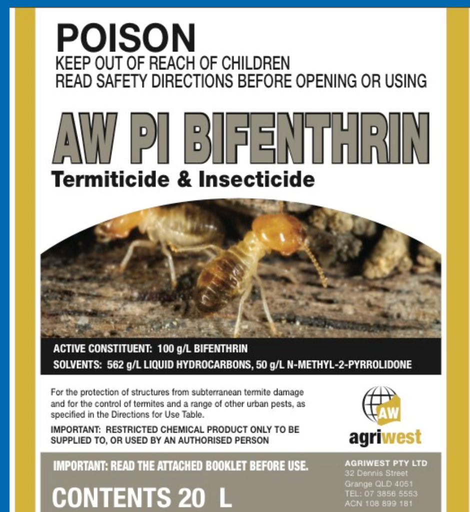
Acknowledgements

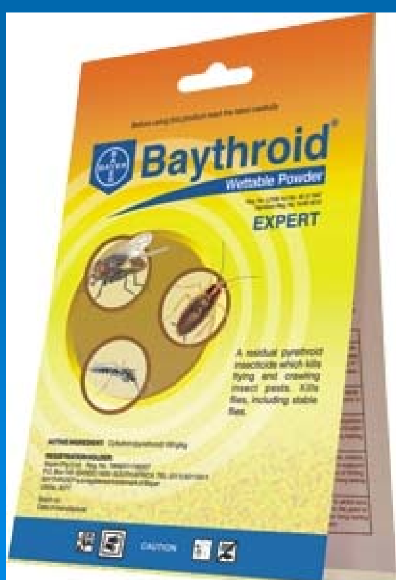
- Funding Sources:
  CALFED Bay Delta Program
  California State Water Resources Control Board
  California Surface Water Ambient Monitoring Program (SWAMP)
  Central Valley Regional Water Quality Control Board
  Hundred Talents Program of the Chinese Academy of Sciences
  Irrigated Lands Program of California
  National Institute for Water Resources
  National Marine Fisheries Service
  National Science Foundation of China
  Orica Ltd
  PRISM Program
  Sacramento Regional County Sanitation District
  University of California – Center for Water Resources
  U.S. Environmental Protection Agency, USEPA STAR Fellowship Program
  U.S. Department of Agriculture
  U.S. Geological Survey National Competitive Grants Program
  U.S. Fish and Wildlife Service Environmental Contaminants Program
  National Marine Fisheries Program

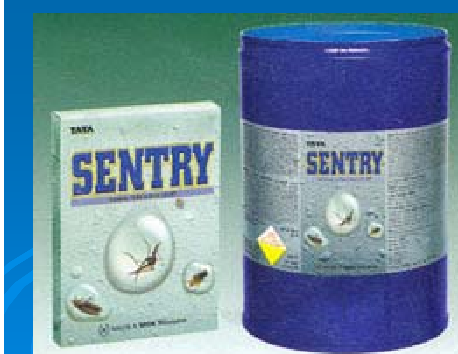
Pyrethroid insecticides

- Synthetic esters derived from the natural chemical pyrethrins
- Non-polar, high K_{ow}, high affinity to sediments
- Replacement of federally-restricted organophosphate insecticides
- Pyrethroids are extremely toxic to aquatic species though pyrethroids have low toxicity to mammals and birds

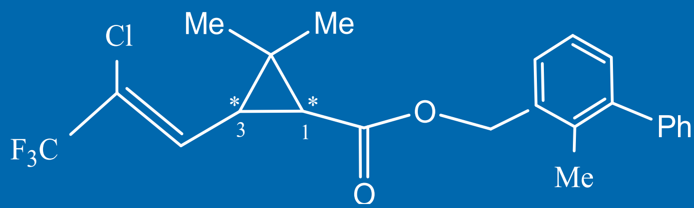
Registered uses



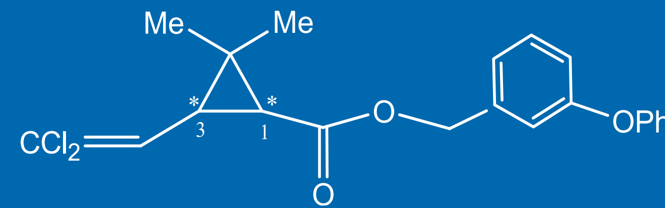




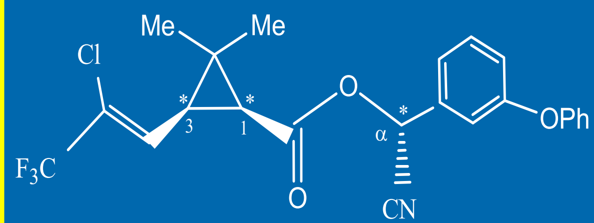
Bifenthrin



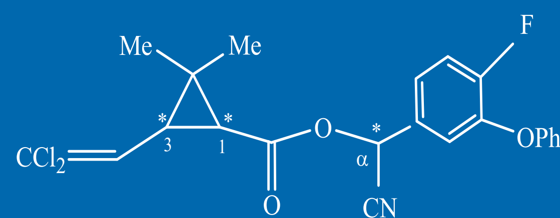
Permethrin



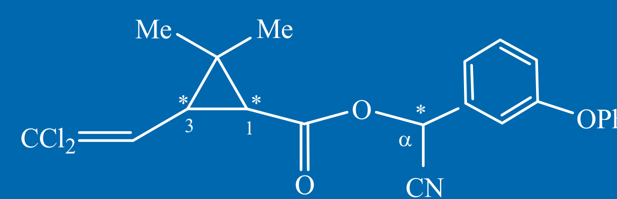
λ-Cyhalothrin



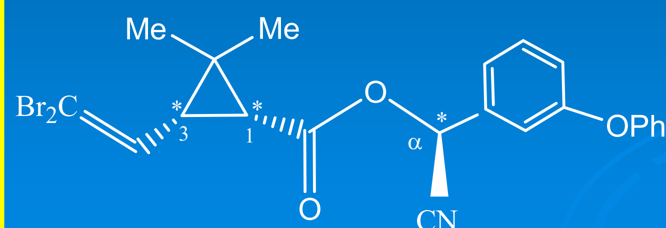
Cyfluthrin



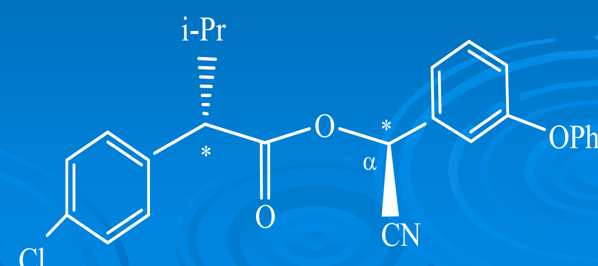
Cypermethrin



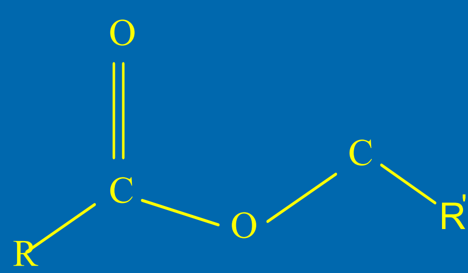
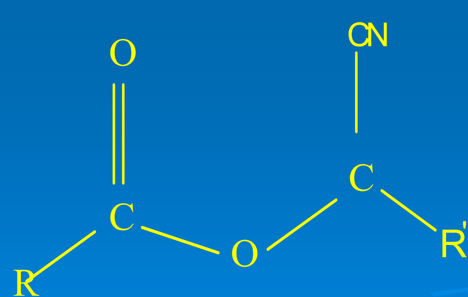
Deltamethrin



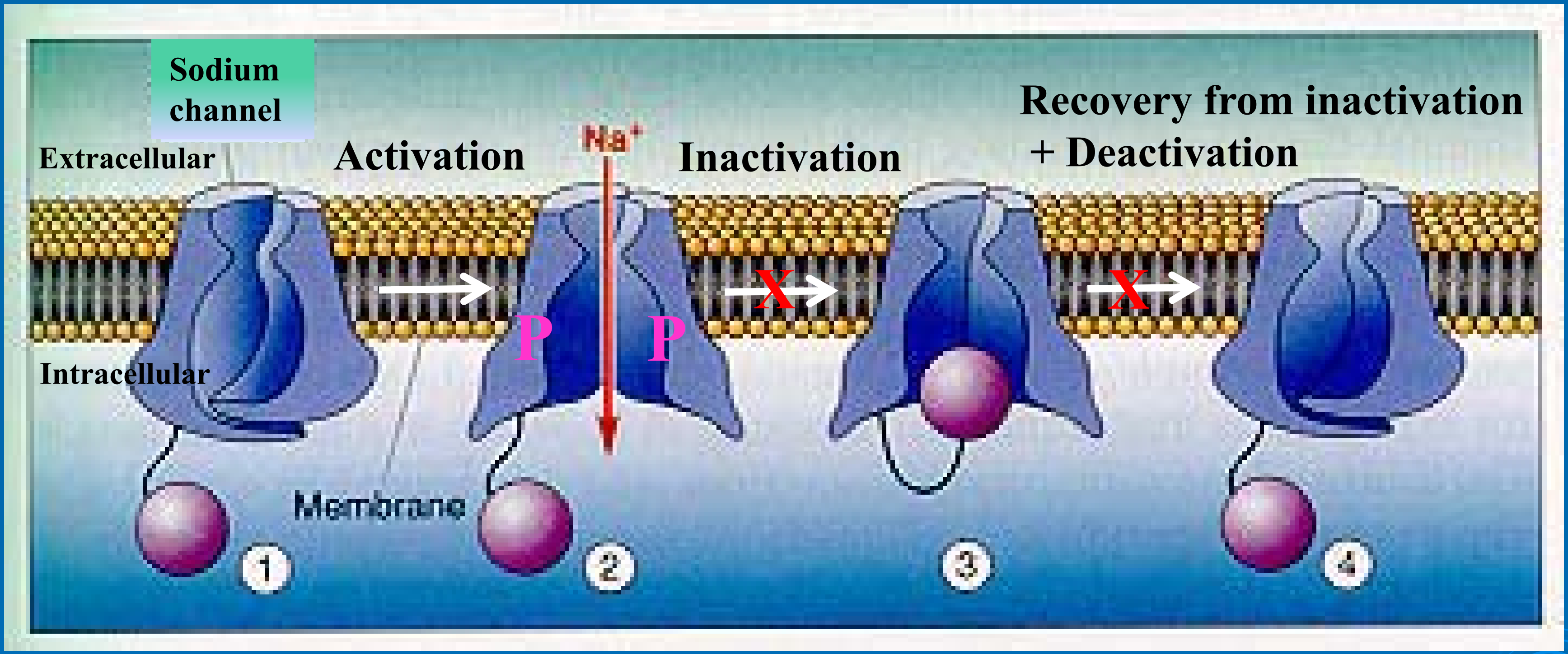
Esfenvalerate



Type of Pyrethroids

	Structure	Chemicals	Toxicity effect
Type I		Bifenthrin, Permethrin	T-syndrome (Tremor)
Type II		Cyfluthrin, λ-Cyhalothrin, Cypermethrin, Deltamethrin, Esfenvalerate	CS-syndrome (choreoathetosis and salivation)

Sodium channels are responsible for the initiation and propagation of action potentials (i.e., electrical impulses)



Pyrethroids prolong the opening of sodium channel resulting in repetitive nerve firing or membrane depolarization

How prevalent are pyrethroids in the environment and are they detected at high enough concentrations to cause harm to non-target species?


California
Central Valley
Urban area in SF Bay & Sacramento
Del Norte
Siskiyou
Modoc
Humboldt
Trinity
Shasta
Lassen
Tehama
Plumas
Glenn
Mendocino
Colusa
Lake
Sutter
Yolo
Placer
Alpine
Calaveras
San Joaquin
Solano
Marin
Sacramento
Contra Costa
San Mateo
Alameda
Santa Cruz
San Benito
Tuolumne
Mono
Inyo
Kings
San Luis Obispo
Kern
Santa Barbara
Ventura
Los Angeles
San Bernardino
Riverside
Orange
San Diego
Imperial


Methods

- 189 total samples in agriculture (106) and urban (83) dominated water bodies. Sediment was collected for toxicity testing and chemical analysis.

- 10-d toxicity tests were conducted with the amphipod, *Hyalella azteca* (only survival data discussed).

- Thirty-one pesticides were determined by GC-ECD (You et al. 2004). The method reporting limit was 1 ppb.

Pyrethroids

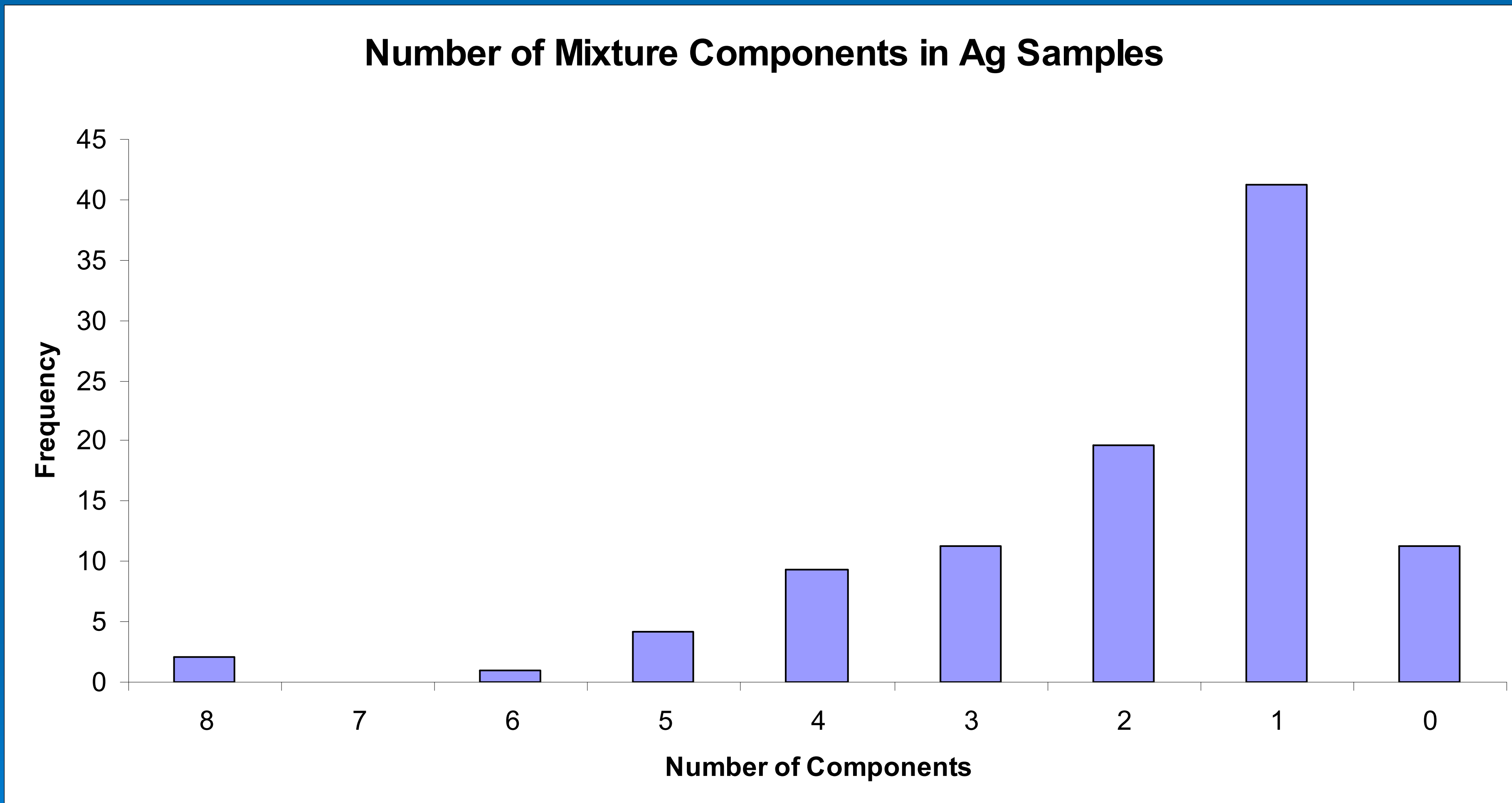
- Bifenthrin
- Cyfluthrin
- Cypermethrin
- Deltamethrin
- Esfenvalerate
- Lambda-cyhalothrin
- Permethrin

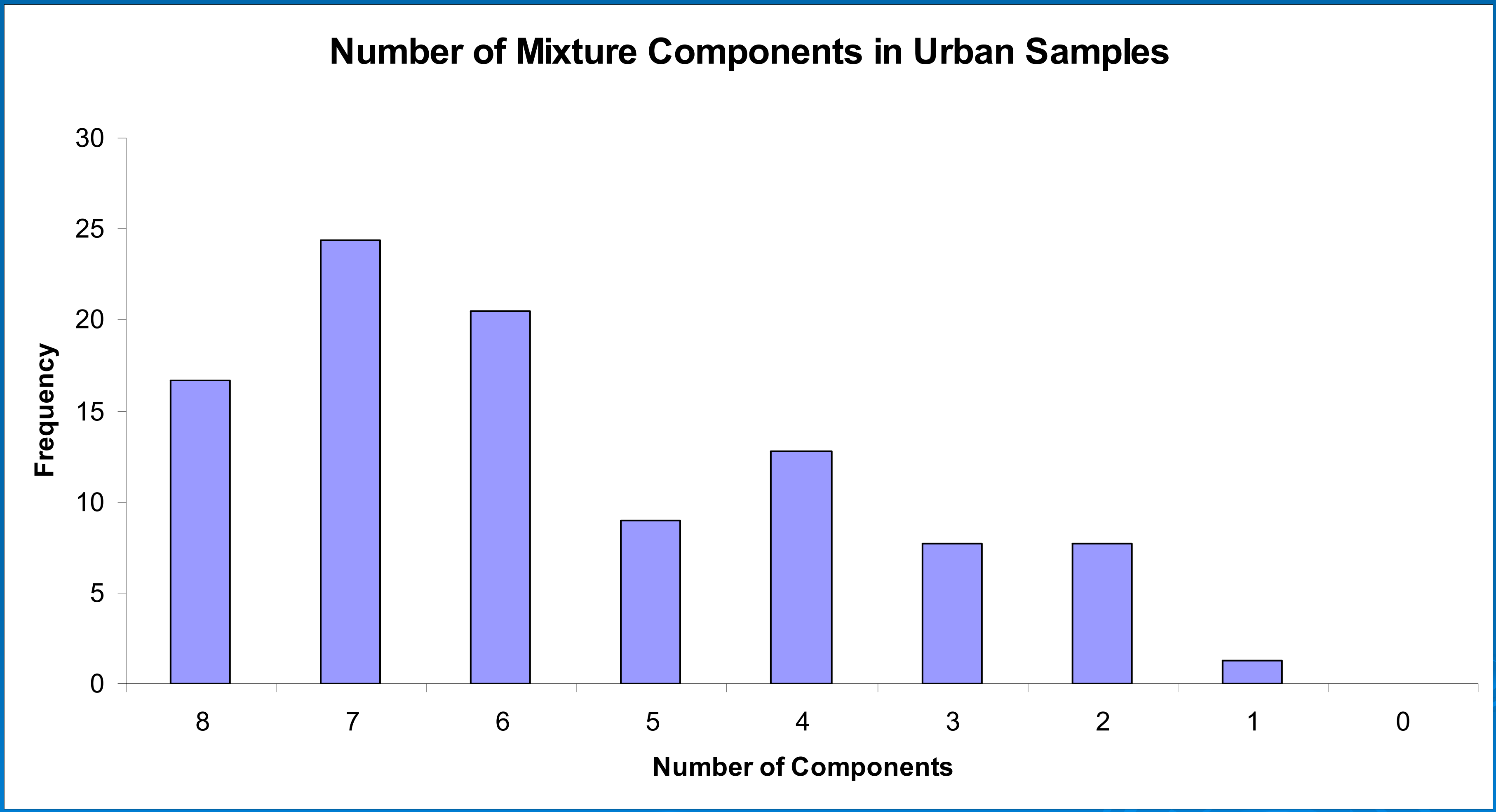
Organophosphates

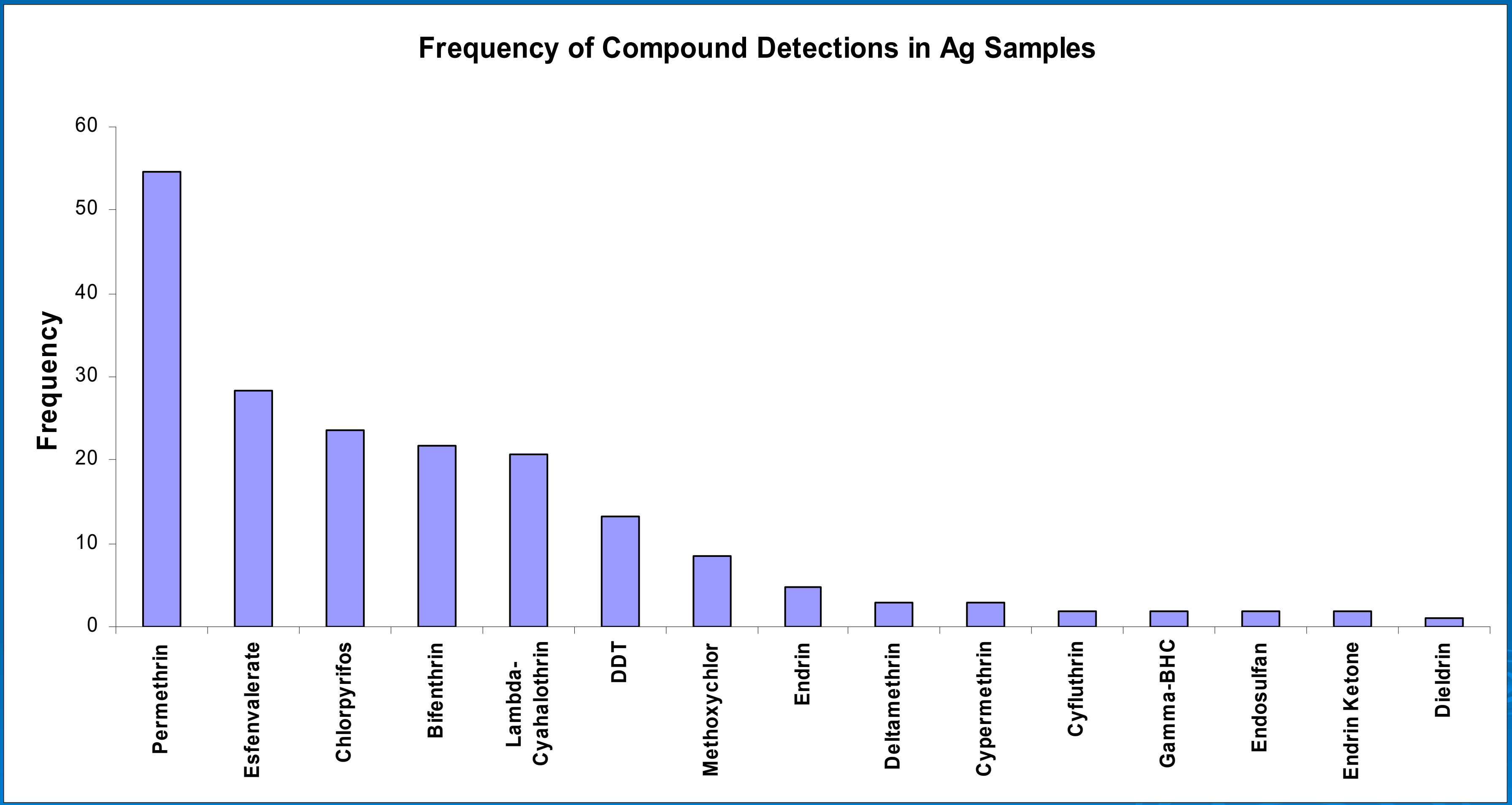
- Chlorpyrifos

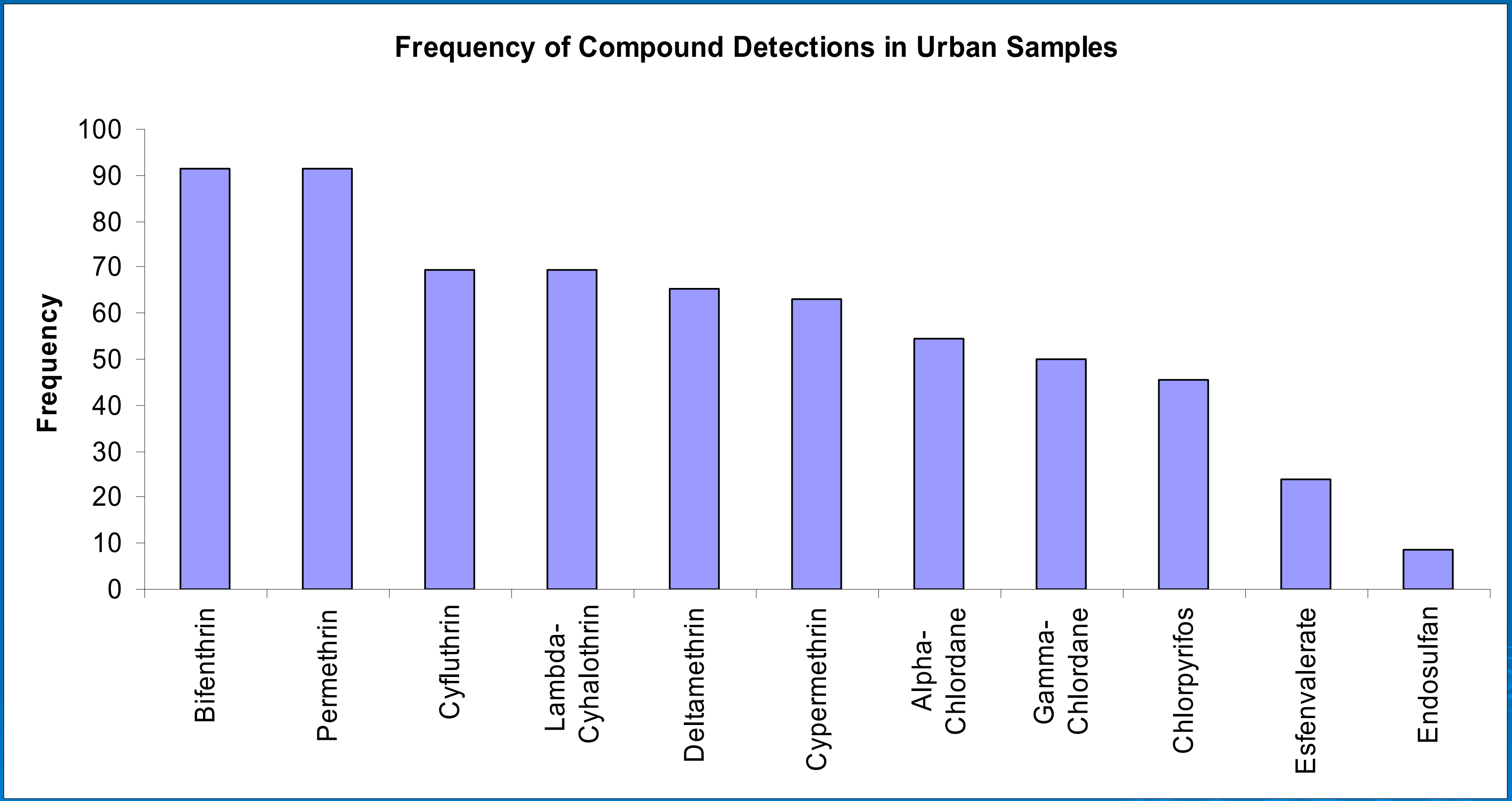
Organochlorines

- Aldrin
- alpha, beta, delta gamma-BHC
- alpha, gamma- chlordane
- DDT, DDE, DDD
- Dieldrin
- Endrin
- Endrin aldehyde
- Endrin ketone
- Endosulfan I, II
- Endosulfan sulfate
- Heptachlor
- Heptachlor epoxide
- Methoxychlor


Number of Mixture Components in Ag Samples
Frequency
45
40
35
30
25
20
15
10
5
0
8
7
6
5
4
3
2
1
0
Number of Components


Number of Mixture Components in Urban Samples
Frequency
30
25
20
15
10
5
0
8
7
6
5
4
3
2
1
0
Number of Components


Frequency of Compound Detections in Ag Samples
Frequency
60
50
40
30
20
10
0
Permethrin
Esfenvalerate
Chlorpyrifos
Bifenthrin
Lambda-Cyahalothrin
DDT
Methoxychlor
Endrin
Deltamethrin
Cypermethrin
Cyfluthrin
Gamma-BHC
Endosulfan
Endrin Ketone
Dieldrin


Frequency of Compound Detections in Urban Samples
Frequency
100
90
80
70
60
50
40
30
20
10
0
Bifenthrin
Permethrin
Cyfluthrin
Lambda-Cyhalothrin
Deltamethrin
Cypermethrin
Alpha-Chlordane
Gamma-Chlordane
Chlorpyrifos
Esfenvalerate
Endosulfan

Dominant pesticides – Frequency of detection

Agricultural sites

- Permethrin (54%)
- Esfenvalerate (28%)
- Chlorpyrifos (24%)
- Bifenthrin (22%)
- Lambda (21%)

Urban sites

- Bifenthrin (91%)
- Permethrin (91%)
- Cyfluthrin (70%)
- Lambda (70%)
- Deltamethrin (65%)
- Cypermethrin (63%)

Sediment 10-d toxicity data

Pyrethroid	Average LC50 (ug/g OC)
lambda-cyhalothrin	0.45
bifenthrin	0.52
deltamethrin	0.79
cyfluthrin	1.08
esfenvalerate	1.54
cypermethrin	1.8
permethrin	10.8

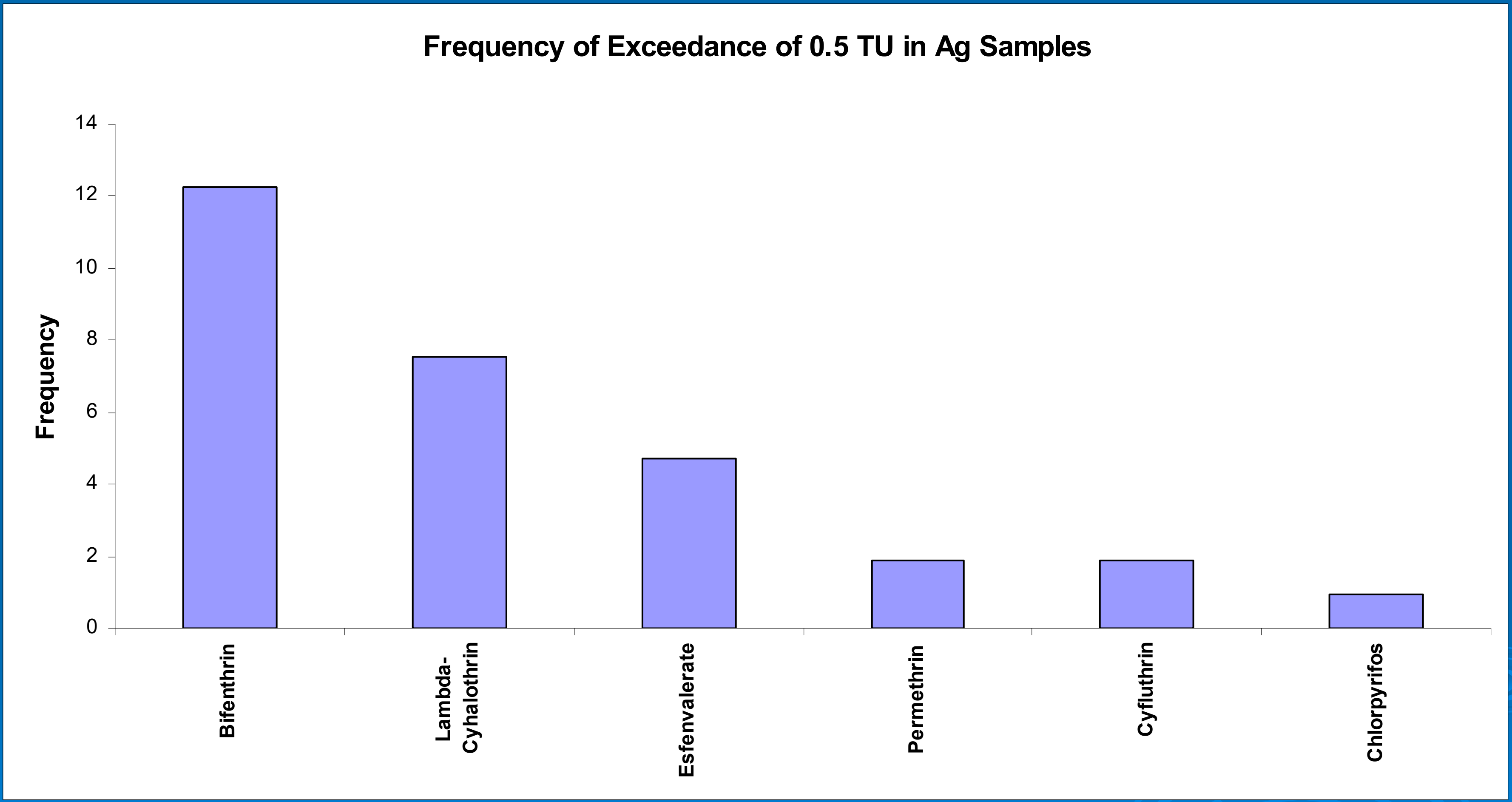
Identifying the contributors to sediment toxicity: TU analysis

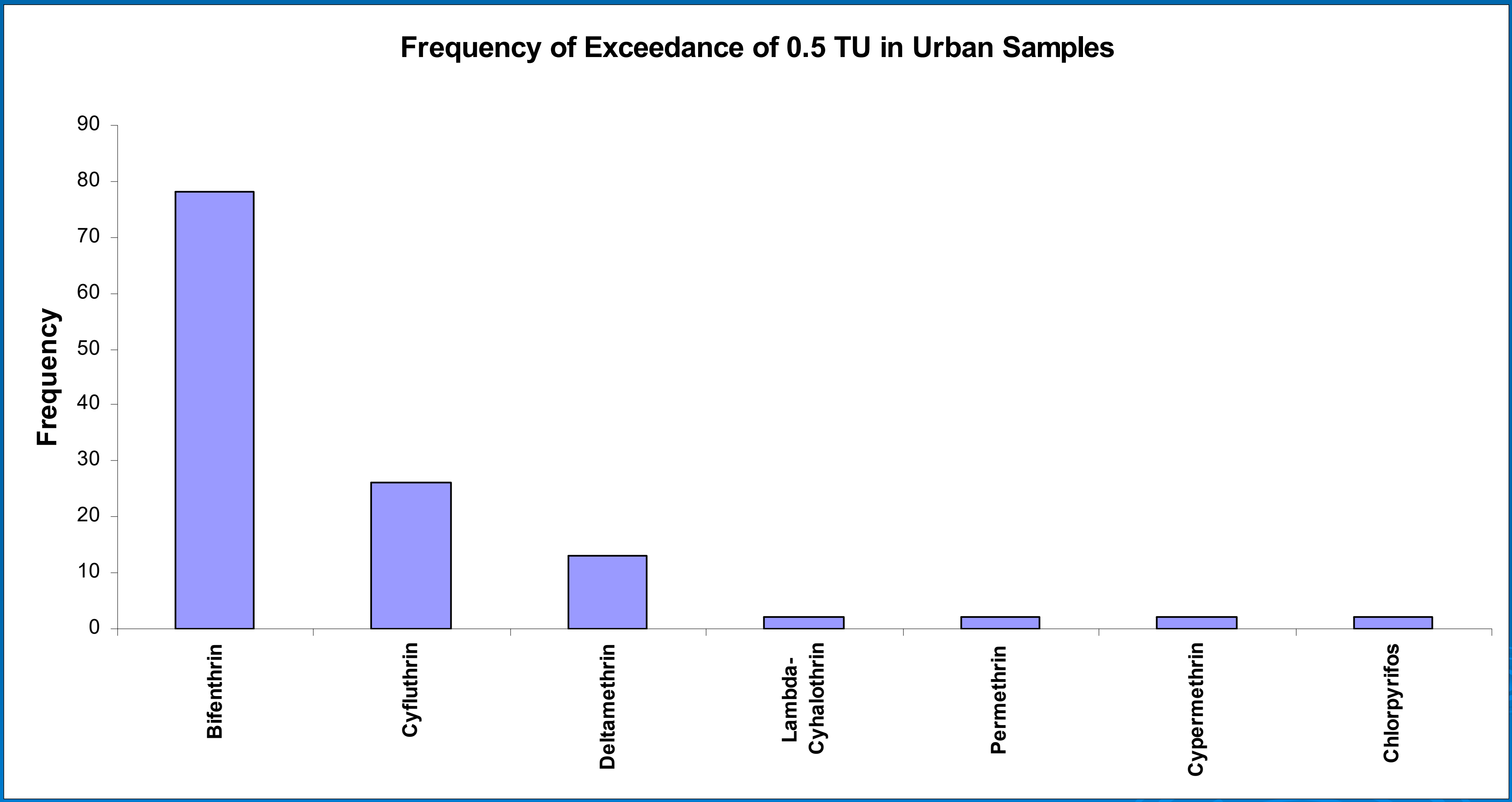
$$\text{Toxicity Unit (TU)} = \frac{\text{Actual conc. in sediment}}{\textit{Hyalella}\ \text{LC50 conc.}}$$

TUs calculated on an organic carbon normalized basis

Assume additivity to get sum of pesticide Tus

Benchmark value = 0.5 TU


Frequency of Exceedance of 0.5 TU in Ag Samples
Frequency
0
2
4
6
8
10
12
14
Bifenthrin
Lambda-Cyhalothrin
Esfenvalerate
Permethrin
Cyfluthrin
Chlorpyrifos



Frequency of Exceedance of 0.5 TU in Urban Samples
Frequency
90
80
70
60
50
40
30
20
10
0
Bifenthrin
Cyfluthrin
Deltamethrin
Lambda-
Cyhalothrin
Permethrin
Cypermethrin
Chlorpyrifos

Dominant pesticides - Risk

Agricultural sites

- Bifenthrin (12%)
- Lambda (8%)
- Esfenvalerate (5%)
- Permethrin (2%)
- Cyfluthrin (2%)
- Chlorpyrifos (1%)

Urban sites

- Bifenthrin (78%)
- Cyfluthrin (26%)
- Deltamethrin (13%)
- Lambda (2%)
- Permethrin (2%)
- Cypermethrin (2%)
- Chlorpyrifos (2%)

Summary

- Complex mixtures of pesticides occur in urban sediments, while simple mixtures occur in agricultural-dominated sites
- Pyrethroid insecticides are the dominant concern in terms of frequency of detects and relative toxicity

Summary

- Pyrethroid concentrations were sufficiently high enough to explain most of the observed toxicity
- Bifenthrin toxicity is greatest in both landscapes (12%, ag sites; 78%, urban sites)
- Other pyrethroids also important (lambda, esfenvalerate, permethrin at ag sites and cyfluthrin, deltamethrin at urban sites)

How prevalent are pyrethroids in the environment and are they detected at high enough concentrations to cause harm to non-target species?

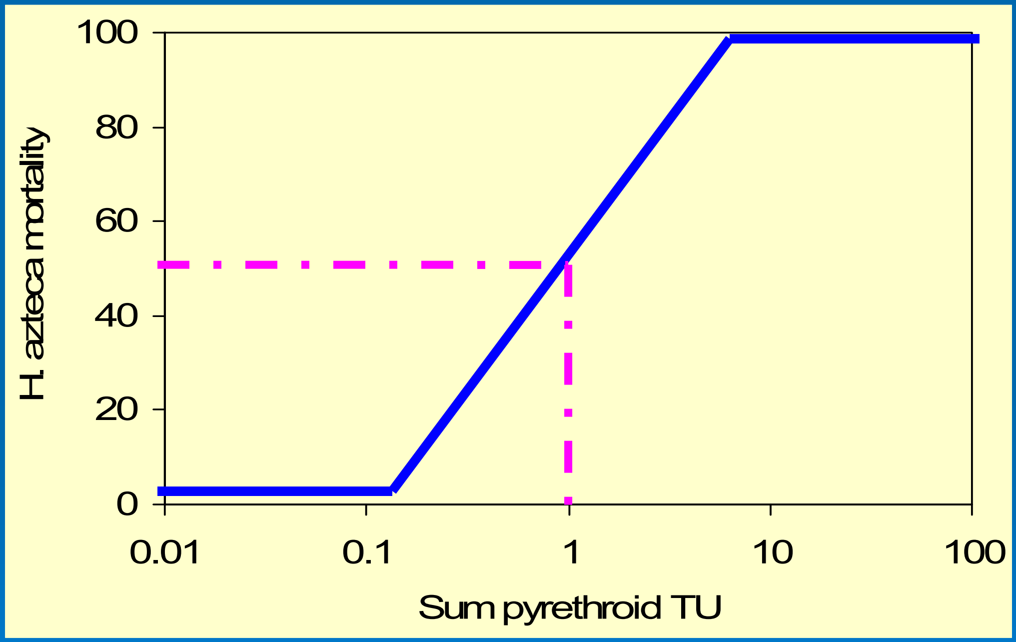
VERY MUCH SO & YES

How do we know its really pyrethroids?

- Quantification
  - Presence does not always equal toxicity
- Toxicity Identification Evaluations

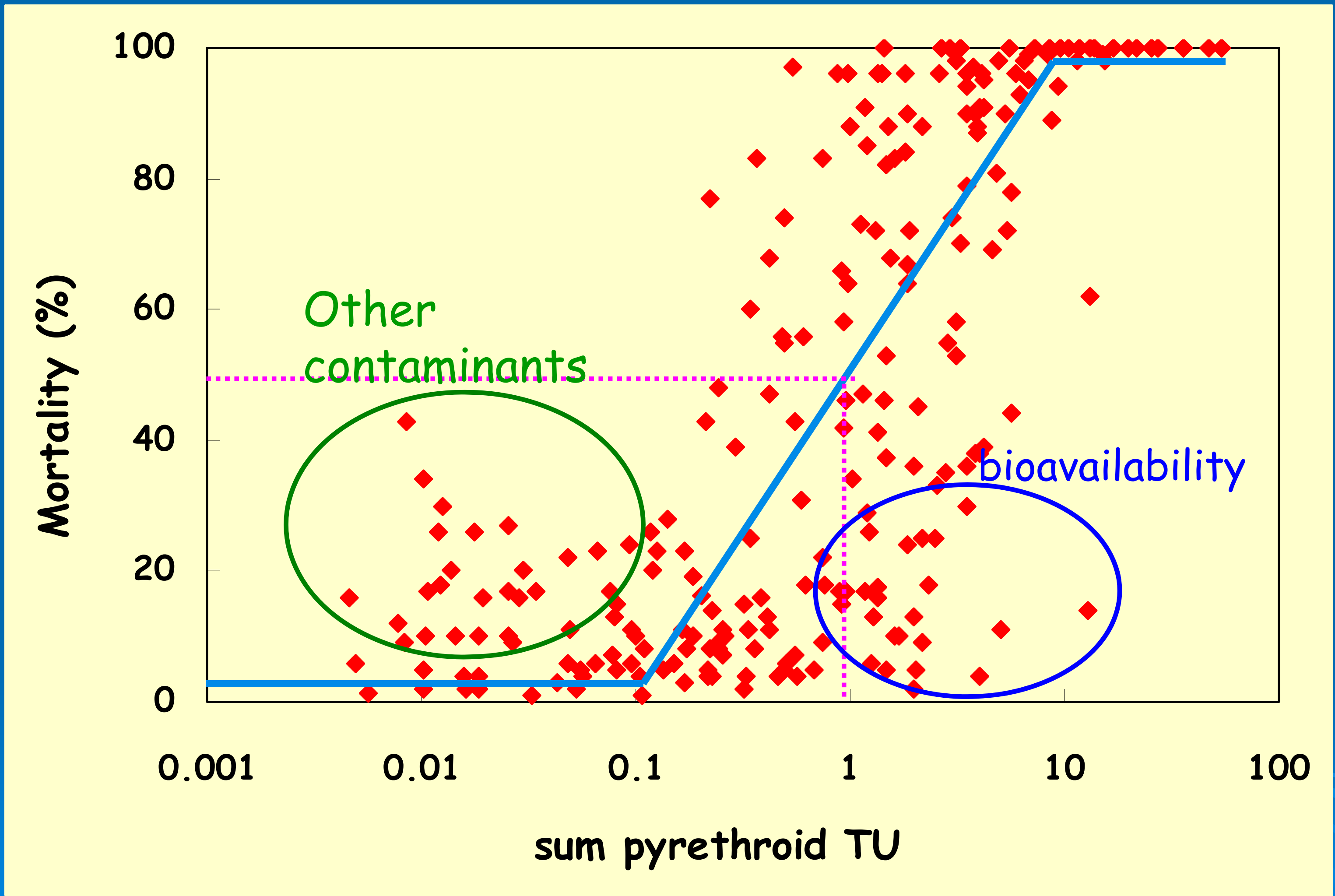
Toxicity unit (TU) – Response Curve

$$TU = \frac{\text{Environmental concentration (OC normalized)}}{\text{10-d } \textit{H. azteca} \text{ LC50 (OC normalized)}}$$



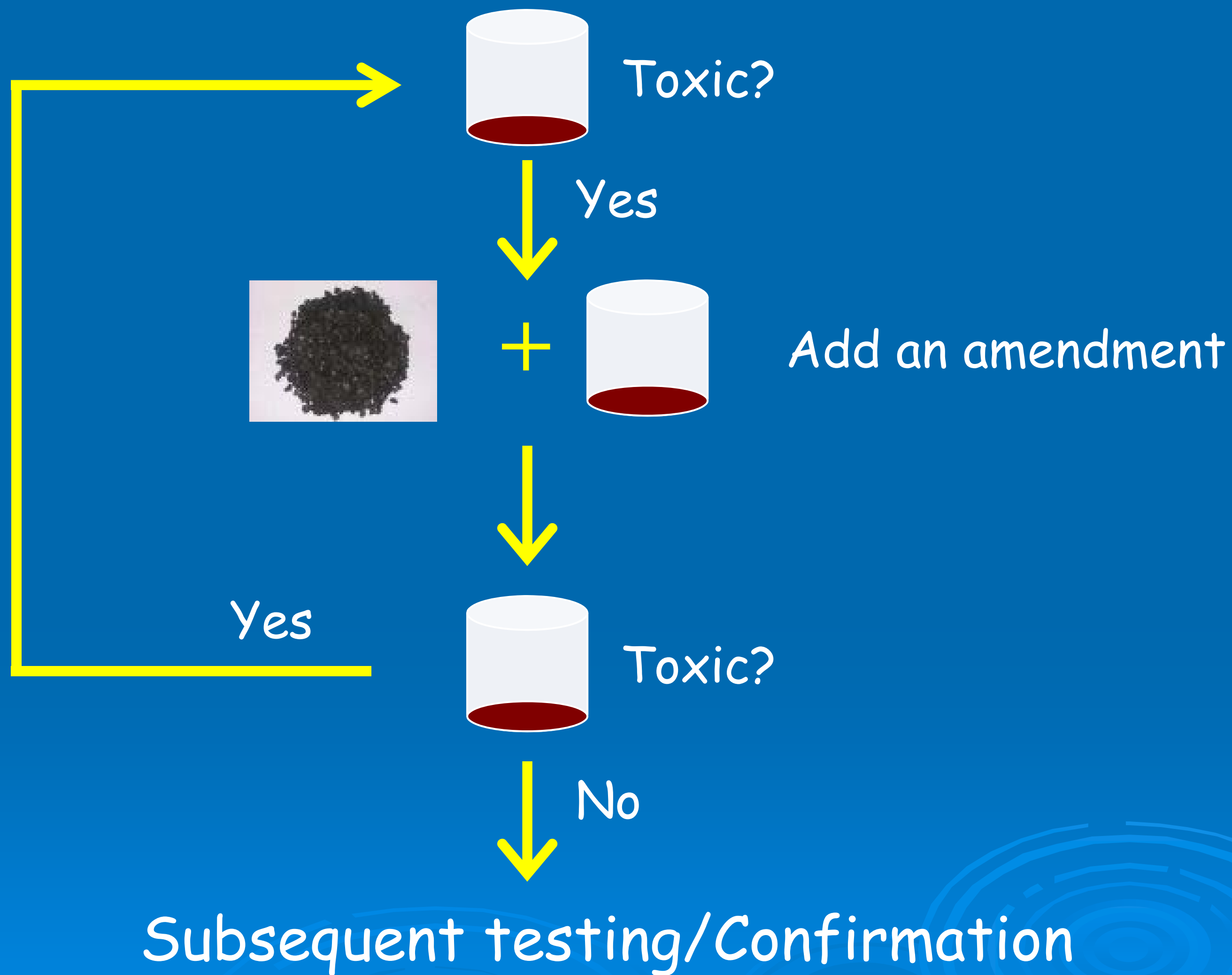
From this equation, 50% mortality will be expected at 1 TU.
Because mode of action for pyrethroids are similar, toxicity is assumed to be additive.

Pyrethroids distribution and sediment toxicity



Sample size: 338, Weston et al. EST 2004, 2005, Amweg et al. EST 2006

Toxicity Identification Evaluations



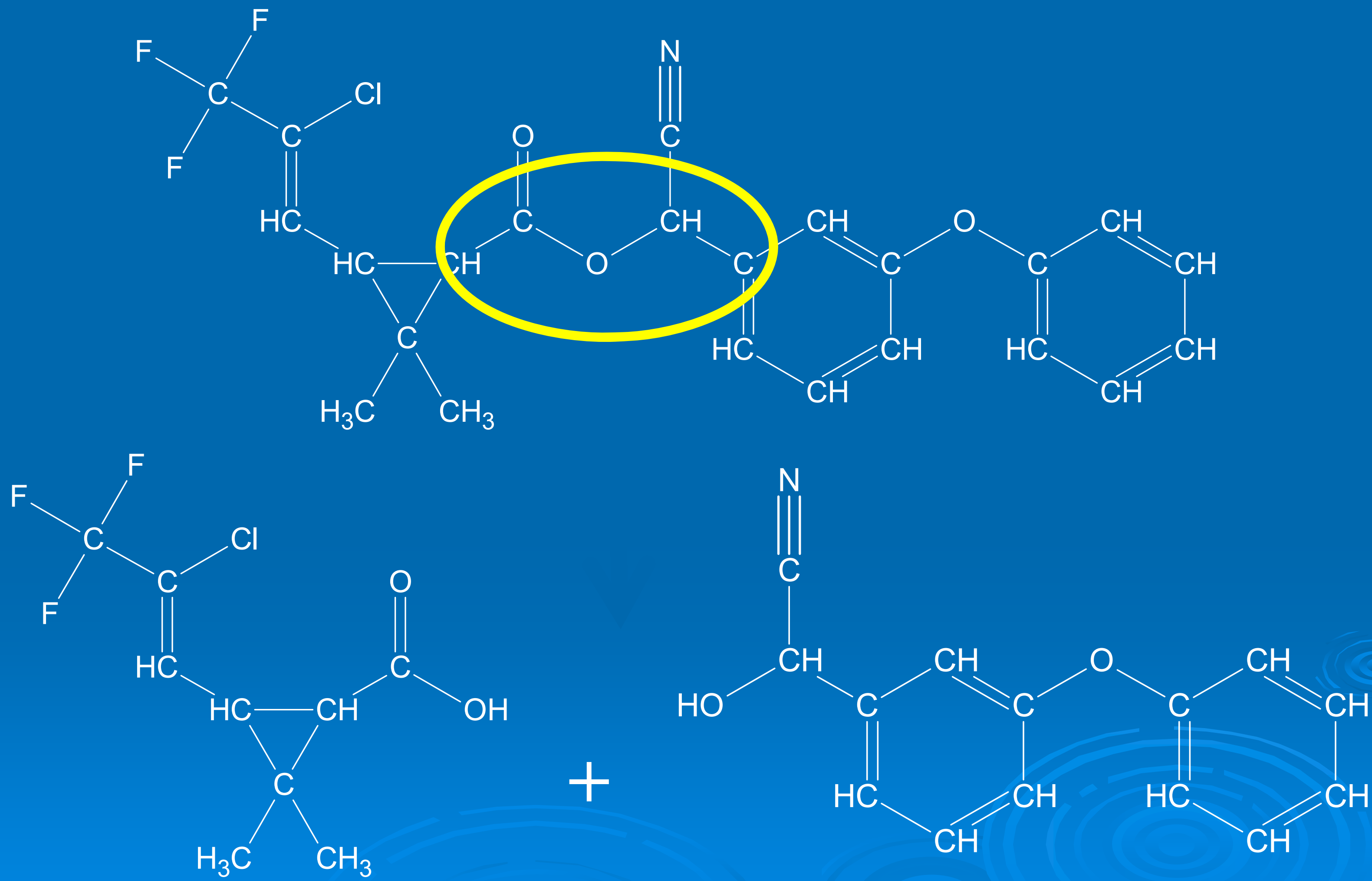
Compound specific TIEs

- Several developed for pyrethroids

1. Esterases
2. PBO
3. Temperature manipulation

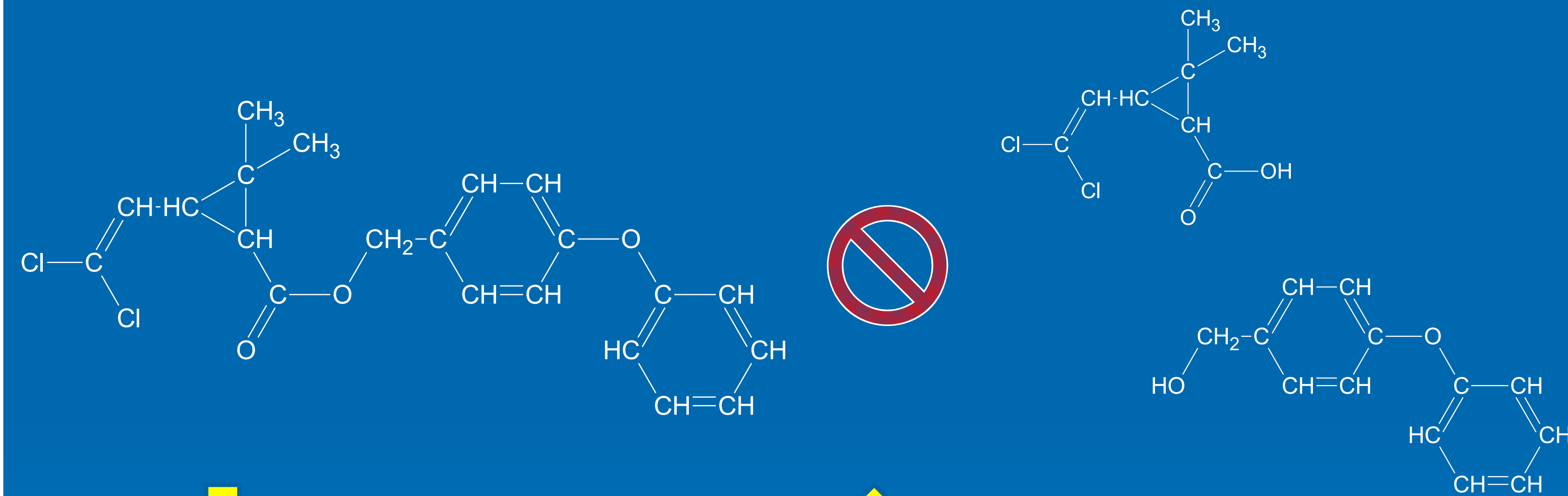
Weston et al. 2009. Environmental Toxicology and Chemistry. 28 (1): 173-180.
Harwood et al. 2009. Environmental Toxicology and Chemistry. 28(5): 1051-1058.
Weston and Lydy. 2010. Chemosphere. 78: 368-374.

Carboxylesterases



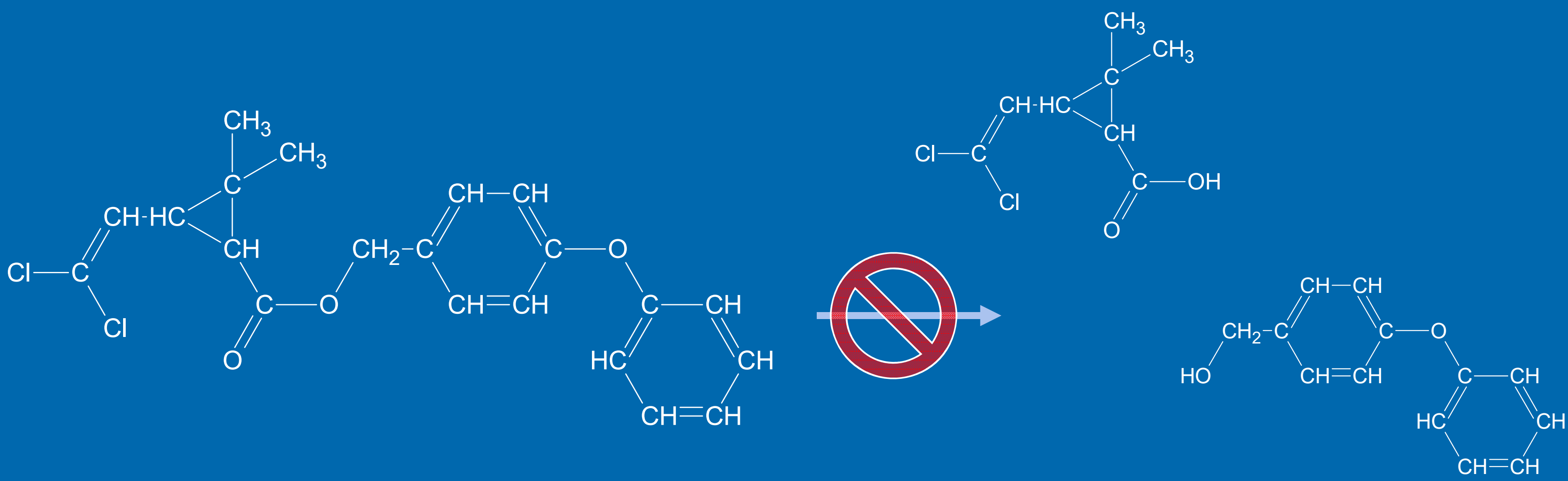
Piperonyl butoxide

Affects the P450 system - decreases biotransformation



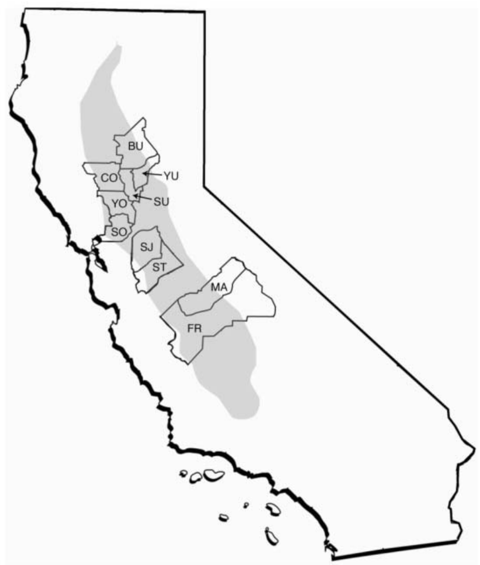
↓ Biotransformation **↑ Toxicity**

Temperature



↓ **Temperature** ↓ **Biotransformation** ↑ **Toxicity**

Are pyrethroid insecticides a California issue only?



SETAC PRESS

Environmental Toxicology and Chemistry, Vol. 29, No. 1, pp. 149–157, 2010

Printed in the USA
DOI: 10.1002/etc.13

DISTRIBUTION AND TOXICITY OF SEDIMENT-ASSOCIATED PESTICIDES IN URBAN AND AGRICULTURAL WATERWAYS FROM ILLINOIS, USA

YUPING DING, AMANDA D. HARWOOD, HEATHER M. FOSLUND, and MICHAEL J. LYDY*
Fisheries and Illinois Aquaculture Center, Department of Zoology, Southern Illinois University, Carbondale, Illinois 62901, USA

(*Submitted* 28 *February* 2009; *Returned for Revision* 24 *April* 2009; *Accepted* 6 *July* 2009)

Environmental Pollution 157 (2009) 110–116

Contents lists available at ScienceDirect

Environmental Pollution

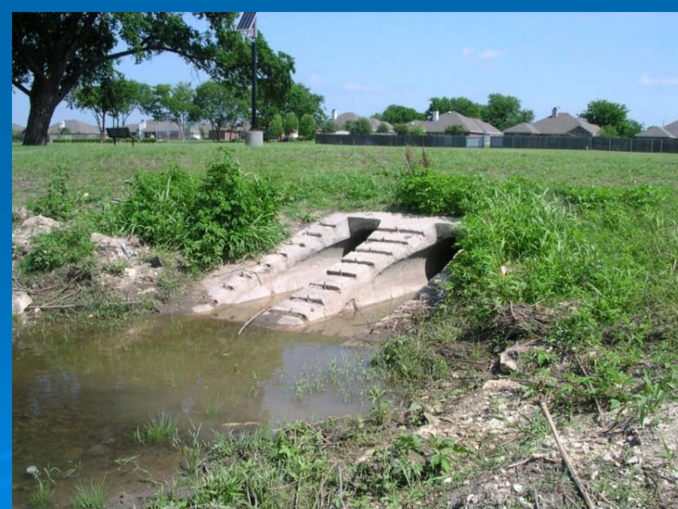
journal homepage: www.elsevier.com/locate/envpol

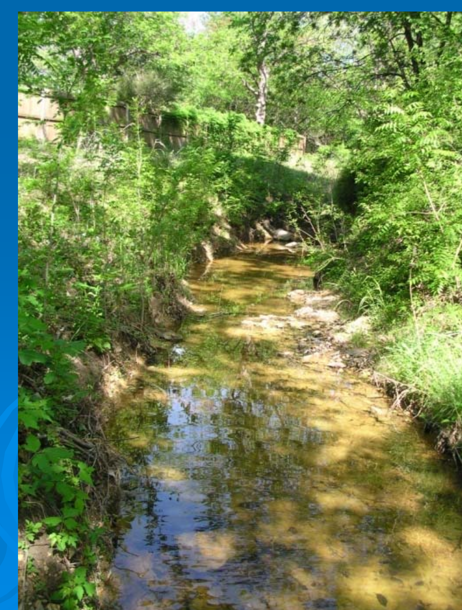
Occurrence and potential toxicity of pyrethroids and other insecticides in bed sediments of urban streams in central Texas

Emily P. Hintzen [a], Michael J. Lydy [b], Jason B. Belden [c,*]

[a] *Department of Environmental Studies, Baylor University, Waco, TX 76798, USA*
[b] *Fisheries and Illinois Aquaculture Center, and Department of Zoology, Southern Illinois University, Carbondale, IL 62091, USA*
[c] *Department of Zoology, Oklahoma State University, 430 Life Science West, Stillwater, OK 74078, USA*

This study examined the presence of insecticides in Texas stream sediments as a model for evaluating the potential impact of urban insecticide use in the Southern United States.





Environmental Science & Technology

Article

pubs.acs.org/est

Occurrence and Potential Sources of Pyrethroid Insecticides in Stream Sediments from Seven U.S. Metropolitan Areas

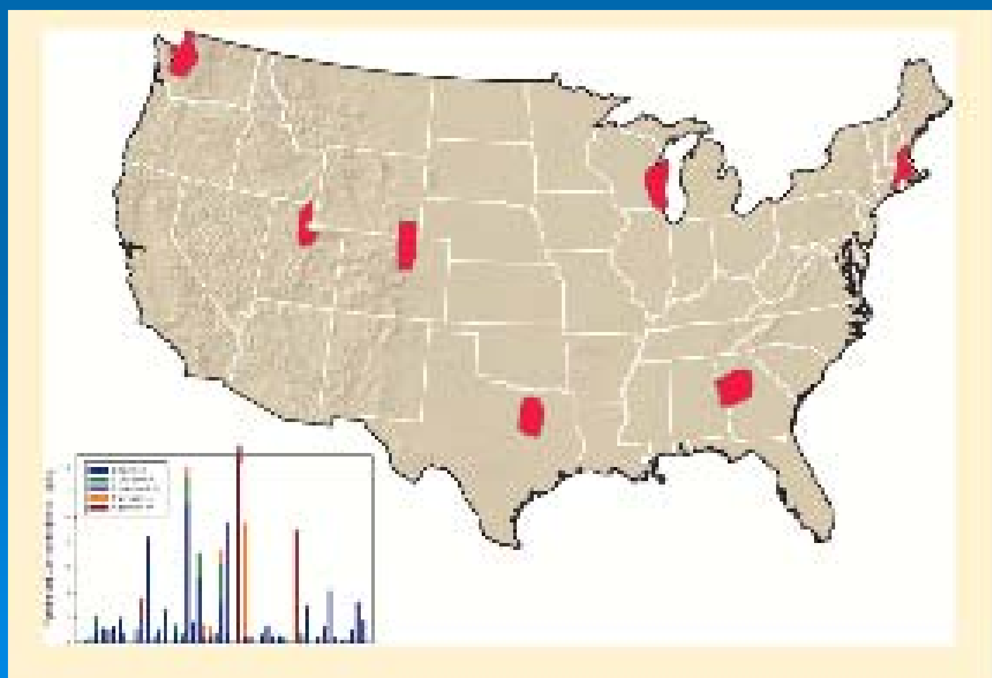
Kathryn M. Kuivila,*,† Michelle L. Hladik,† Christopher G. Ingersoll,‡ Nile E. Kemble,‡ Patrick W. Moran, Daniel L. Calhoun, Lisa H. Nowell,† and Robert J. Gilliom†

†California Water Science Center, U.S. Geological Survey, Sacramento, California, United States

‡Columbia Environmental Research Center, U.S. Geological Survey, Columbia, Missouri, United States

Washington Water Science Center, U.S. Geological Survey, Tacoma, Washington, United States

Georgia Water Science Center, U.S. Geological Survey, Atlanta, Georgia, United States



Chemosphere 82 (2011) 1373–1379

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Occurrence and distribution of sediment-associated insecticides in urban waterways in the Pearl River Delta, China

Huizhen Li [a,b], W. Tyler Mehler [a,c], Michael J. Lydy [c], Jing You [a,*]

[a] *State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China*
[b] *Graduate School of the Chinese Academy of Sciences, Beijing 100049, China*
[c] *Fisheries and Illinois Aquaculture Center and Department of Zoology, Southern Illinois University, 171 Life Science II, Carbondale, IL 62901, USA*

Where are the pyrethroids, and particularly bifenthrin, coming from in general?

Lawn care products available

Granular products

- Scott's Turf Builder with Summerguard (BIFENTHRIN)
- Ortho Basic Solutions Lawn and Garden Insect Killer (BIFENTHRIN)
- Ortho Bug-B-Gon Max Insect Killer for Lawns (BIFENTHRIN)
- Spectracide Triazide Soil and Turf Insect Killer (LAMBDA-CYHALOTHRIN)

Liquid concentrates

- Ortho Bug-B-Gon Max Lawn and Garden Insect Killer (ESFENVALERATE)
- Ortho Basic Solutions Lawn and Garden Insect Killer (liquid) (PERMETHRIN)

Some surprising numbers

Assume:

Use of Ortho Bug-B-Gon Max Insect Killer for Lawns
(or any of several similar products)

Application to lawn using a spreader at the recommended rate

A modest size lawn of 30 ft by 30 ft

Loss of 1% of the applied amount in runoff (= 8 mg bifenthrin)

How much would that 8 mg bifenthrin have to be diluted before it was no longer acutely toxic to Hyalella?

If diluted in sediment:

3 tons of sediment

(wet weight; assuming 2% organic carbon and 60% solids content)

If diluted in water:

1 million gallons

The source…

PNAS

Multiple origins of pyrethroid insecticide resistance across the species complex of a nontarget aquatic crustacean, *Hyalella azteca*

Donald P. Weston[a,1], Helen C. Poynton[b], Gary A. Wellborn[c], Michael J. Lydy[d], Bonnie J. Blalock[b], Maria S. Sepulveda[e], and John K. Colbourne[f]

[a]Department of Integrative Biology, University of California, Berkeley, CA 94720; [b]School for the Environment, University of Massachusetts, Boston, MA 02125; [c]Department of Biology, University of Oklahoma, Norman, OK 73019; [d]Center for Fisheries, Aquaculture and Aquatic Sciences, Southern Illinois University, Carbondale, IL 62901; [e]Department of Forestry and Natural Resources, Purdue University, West Lafayette, IN 47907; and [f]The Center for Genomics and Bioinformatics, Indiana University, Bloomington, IN 47405

Another problem…..

We and others have found locations from which the sediment and/or water are highly toxic due to pyrethroid insecticides when tested with *H. azteca* in the lab, yet the sites contain a thriving wild population of *H. azteca*.

Toxicity of the pyrethroids to wild populations of *Hyalella azteca*

Species Group	Collection Site	Cyfluthrin 96-h LC_{50} (ng/L)	Relative Tolerance
Lab cultures			
C	UCB	4.8 (3.9-6.2)	1
Wild Populations			
A	Laguna Lake (LL)	4.8 (3.7-5.8)	1
B	Blodgett Reservoir (BR)	1.3 (1.1-1.5)	1
	Pleasant Grove Creek (PG)	11.8 (8.8-14.7)	3
D	Morrison Creek (MO)	132 (63.5-174)	30
	Mosher Slough (MS)	211 (176-244)	50
	Grayson Creek (GC)	>691	>175
	Chualar Creek (CH)	535 (403-650)	100

Mechanism of pyrethroid resistance

The resistant H. azteca populations have achieved resistance by mutations in the voltage-gated sodium channel gene, found on chromosome 3.

UCB animals - A portion of chromosome 3, and the encoded amino acid sequence

Proline Threonine Leucine Asparagine Leucine Leucine Isoleucine Serine Isoleucine Methionine Glycine Lysine Threonine Valine Glycine Alanine Leucine Glycine

……CCCACGCTCAACTTGCTCATCTCCATCATGGGCAAGACGGTGGGTGCCCTCGGC……

Resistant *H. azteca* populations contained one or both of these mutations

Leucine

.......TTG.......

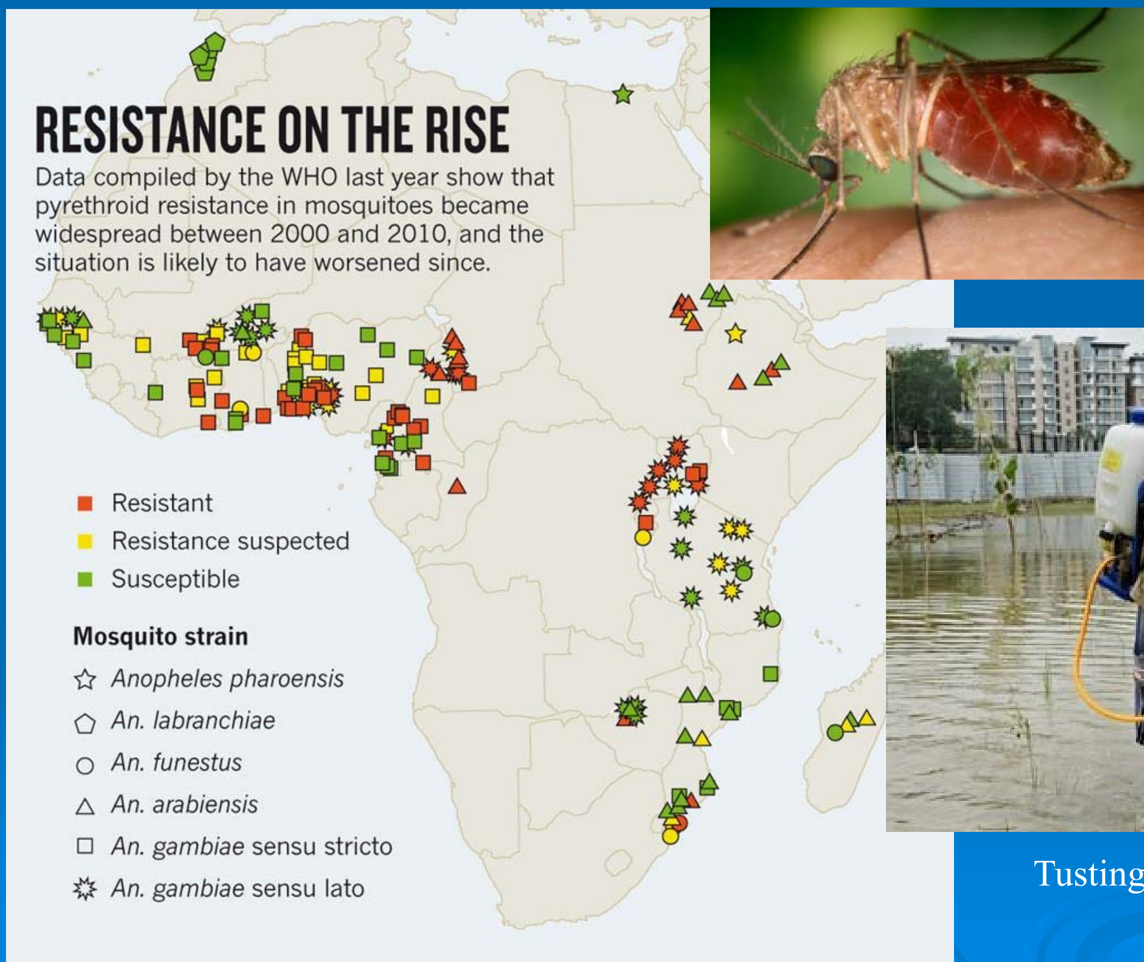
918 - Well known mutation in insects, known as super-kdr "*super-knock down resistance*"

Isoleucine

......ATC......

925 - Mutation previously found in white fly

Resistance in vector species is common



Tusting, L. *The Guardian*. Feb 2014

Nature 475, 19 (2011)

Controversy – Adaptation or Acclimation?

SETAC PRESS

Environmental Toxicology and Chemistry, Vol. 34, No. 10, pp. 2250–2262, 2015

Printed in the USA

Environmental Toxicology

COMPARATIVE SENSITIVITY OF FIELD AND LABORATORY POPULATIONS OF *HYALELLA AZTECA* TO THE PYRETHROID INSECTICIDES BIFENTHRIN AND CYPERMETHRIN

Stephen L. Clark,*† R. Scott Ogle,† Andrew Gantner,† Lenwood W. Hall Jr.,‡ Gary Mitchell,§ Jeffrey Giddings,|| Matthew McCoole,# Michael Dobbs,†† Kevin Henry,‡‡ and Ted Valenti‡‡

†Pacific EcoRisk, Fairfield, California, USA
‡University of Maryland, Queenstown, Maryland, USA
§FMC Agricultural Products, Ewing, New Jersey, USA
||Compliance Services International, Rochester, Massachusetts, USA

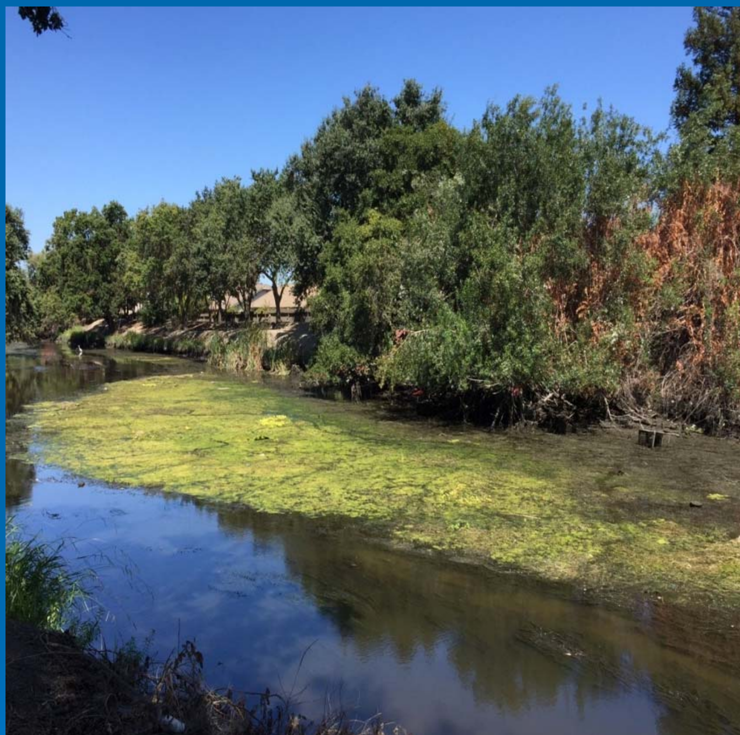
- Clark et al. reported LC50 values 49 and 300 times greater for cypermethrin and bifenthrin in field-collected *Hyalella* compared to lab populations
- Lost partial tolerance over time – attributed to non-genetic enzyme activity
- Did not measure genetic VGSC mutations as noted in Weston et al. (2013)
- **Is resistance maintained when animals are cultured long-term in a pyrethroid-free environment?**

Slide 48

JH5 2013

Jennifer Heim, 2/3/2017

Mosher Slough – Stockton, CA



D-clade resistant
cultured since December, 2013

U.S. EPA Lab – Duluth, MN

C-clade non-resistant
cultured since 2001

Toxicity Bioassays

- RES *Hyalella* tested after 14, 22 and 30 months in culture
- NR *Hyalella* also tested
- EPA protocol 600/R-99/064
- 96-h static water-only exposures to permethrin
- Lethality endpoint
- Probit analysis to determine LC50

X 10

Population	Test Date	LC50 (95% Confidence Intervals)
Non-Resistant	June 2015	34.5 ng/L (31.3 – 38.3)[a]
Non-Resistant	October 2015	31.2 ng/L (26.4 – 36.9)[a]
Resistant	July 2015 (14 months in culture)	1140 ng/L (942 – 1390)[b]
Resistant	February 2016 (22 months in culture)	1670 ng/L (1380 – 2010)[b]
Resistant	October 2016 (30 months in culture)	1418 ng/L (1269 - 1585)[b]

- Approximately 53-fold decreased sensitivity to permethrin that is retained over time.
- So was this result due to the mutation being maintained in the population ?

YES… Resistant *Mosher Slough* population retained the L925 mutation after 16 months!

UCB animals - A portion of chromosome 3, and the encoded amino acid sequence

Proline Threonine Leucine Asparagine Leucine Leucine Isoleucine Serine Isoleucine Methionine Glycine Lysine Threonine Valine Glycine Alanine Leucine Glycine

……CCCACGCTCAACTTGCTCATCTCCATCATGGGCAAGACGGTGGGTGCCCTCGGC……

Resistant *H. azteca* populations contained one or both of these mutations

Leucine

…….TTG…….

Isoleucine

……ATC……

918 - Well known mutation in insects, known as super-kdr "*super-knock down resistance*"

925 - Mutation previously found in white fly

Adaptation or Acclimation?

- Mosher Slough *H. azteca* are permanently genetically altered (presence of L925I and L925V)

  Adaptation

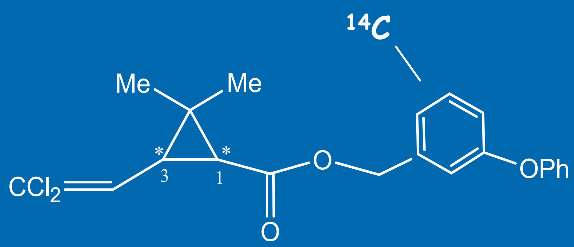
- Mosher Slough *H. azteca* maintained pyrethroid resistance when cultured in a pyrethroid-free environment (LC50 at 30 months ~ 50 times non-resistant animals)

  Adaptation

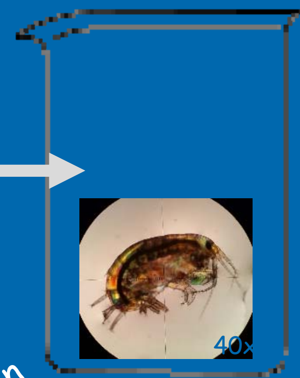
- Acclimation is also involved, but it is not a heritable trait.

Does this resistance have an impact on bioaccumulation of pyrethroids?

Methods



^{14}C-labeled permethrin
55% cis/45% trans



Water Exposure,
7-14 d old *H. azteca*

Tissue Homogenization

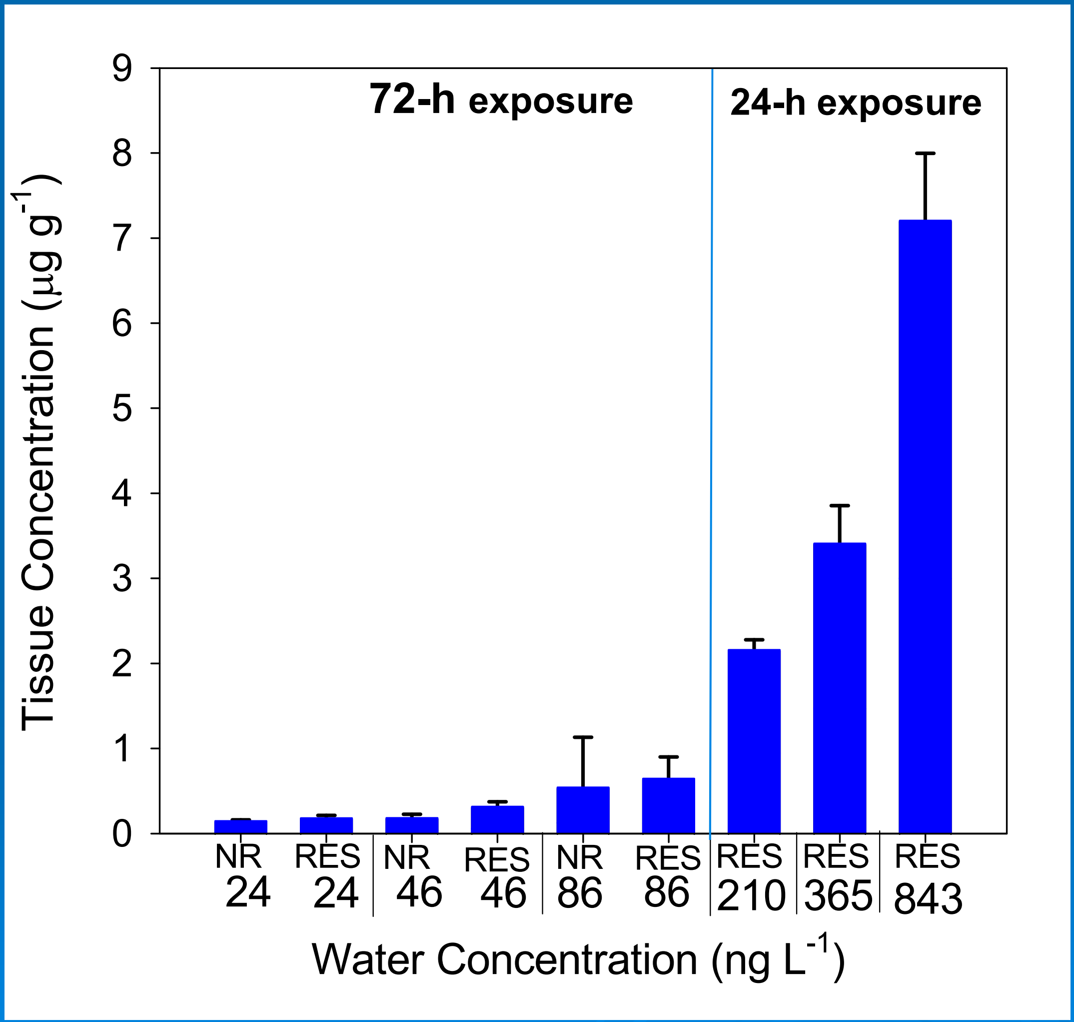
Subsample of tissue

Packard TriCarb 2900TR LSC

Separate fractions for parent permethrin and biotransformation products

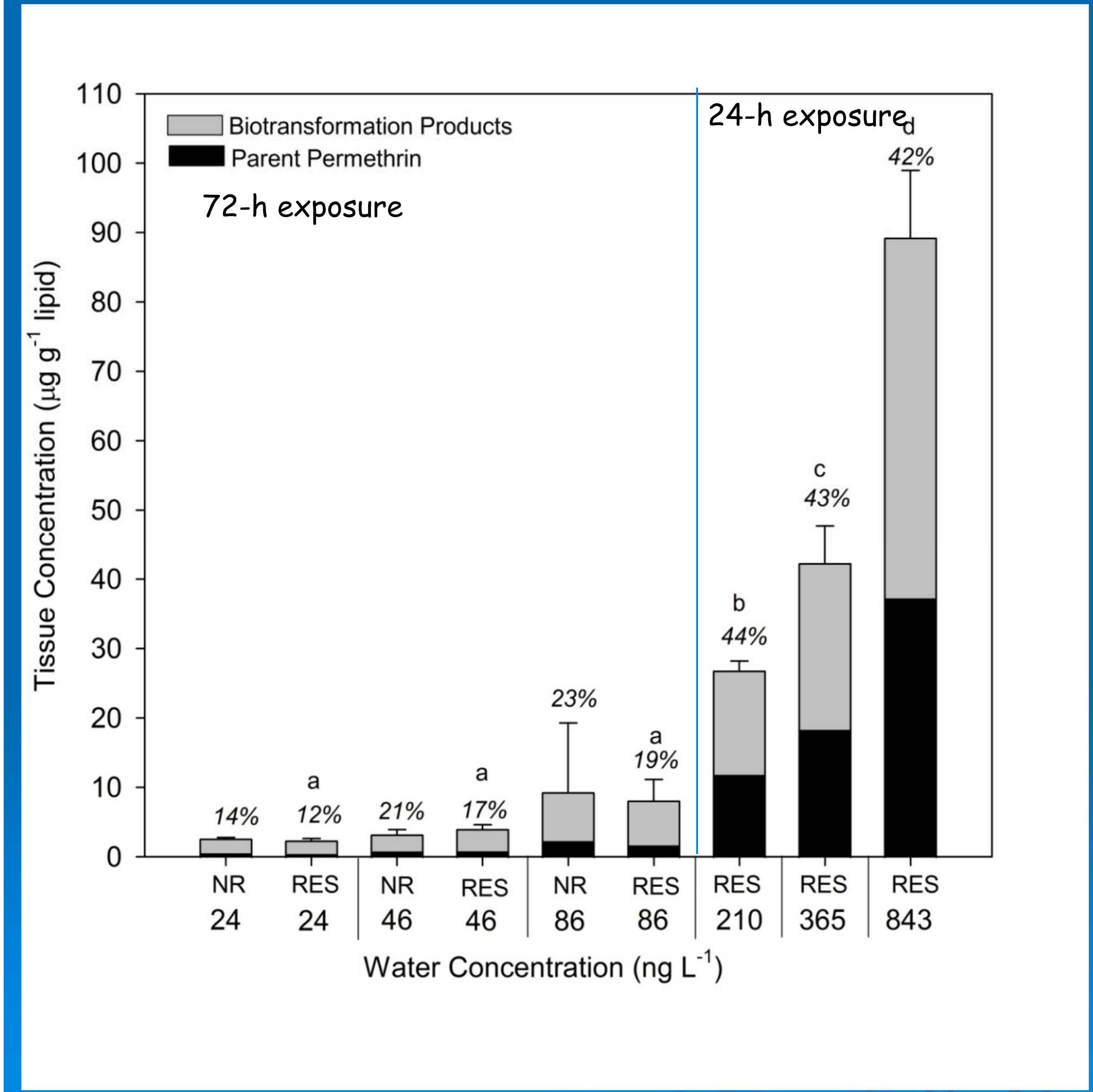
Agilent 1100 HPLC equipped with fraction collector

Permethrin Bioaccumulation



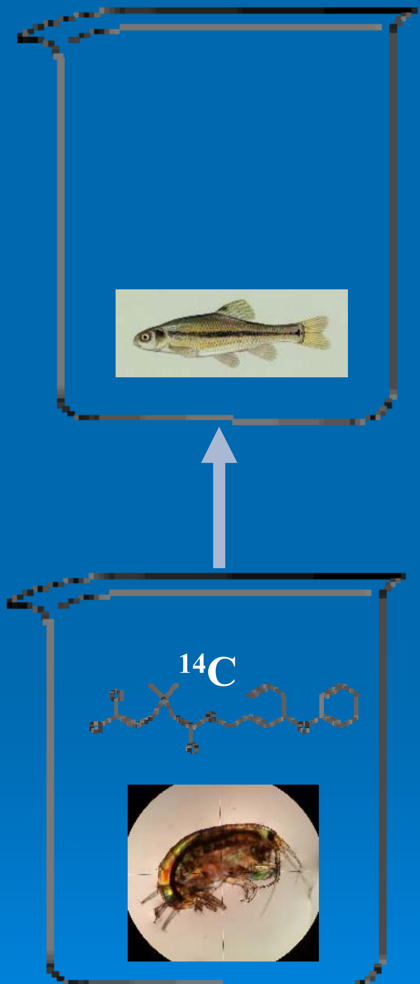
- Similar bioaccumulation of total permethrin in NR & RES *H. azteca.*
- RES *H. azteca* bioaccumulation increased as the permethrin exposure concentration increased.

Permethrin Biotransformation



- Similar biotransformation proportions were noted in NR & RES *H. azteca*
- As the exposure concentration increased, proportion of permethrin biotransformed decreased.

Potential for Permethrin Trophic Transfer

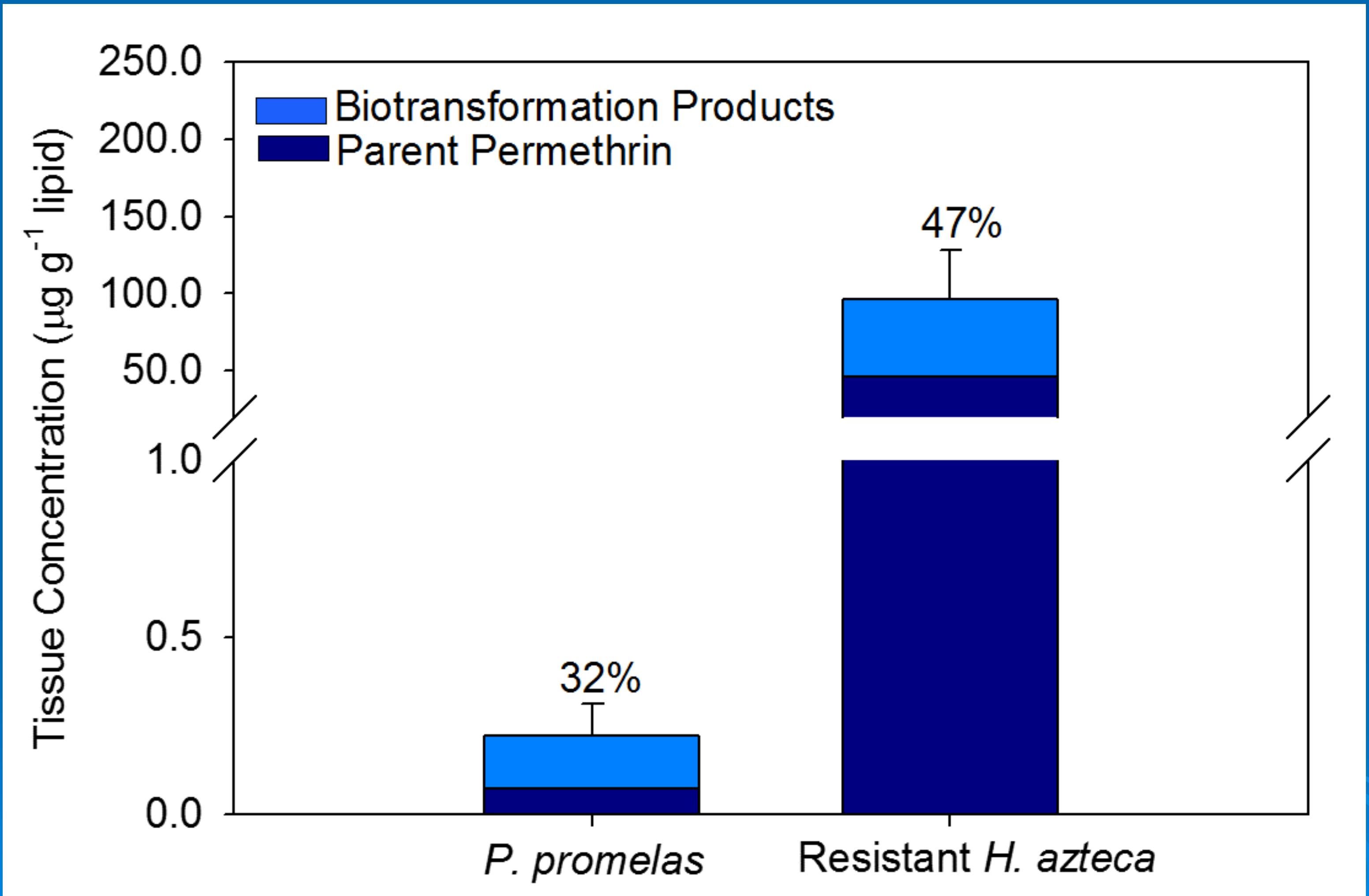


- *Pimephales promelas* fed for 4 days
- Static renewal system

- 15 *Hyalella* fed to each fish/day

- 15 *H. azteca*
- Water spiked at 780 ng/L
- Exposed for 24 h

Potential for Permethrin Trophic Transfer



Findings

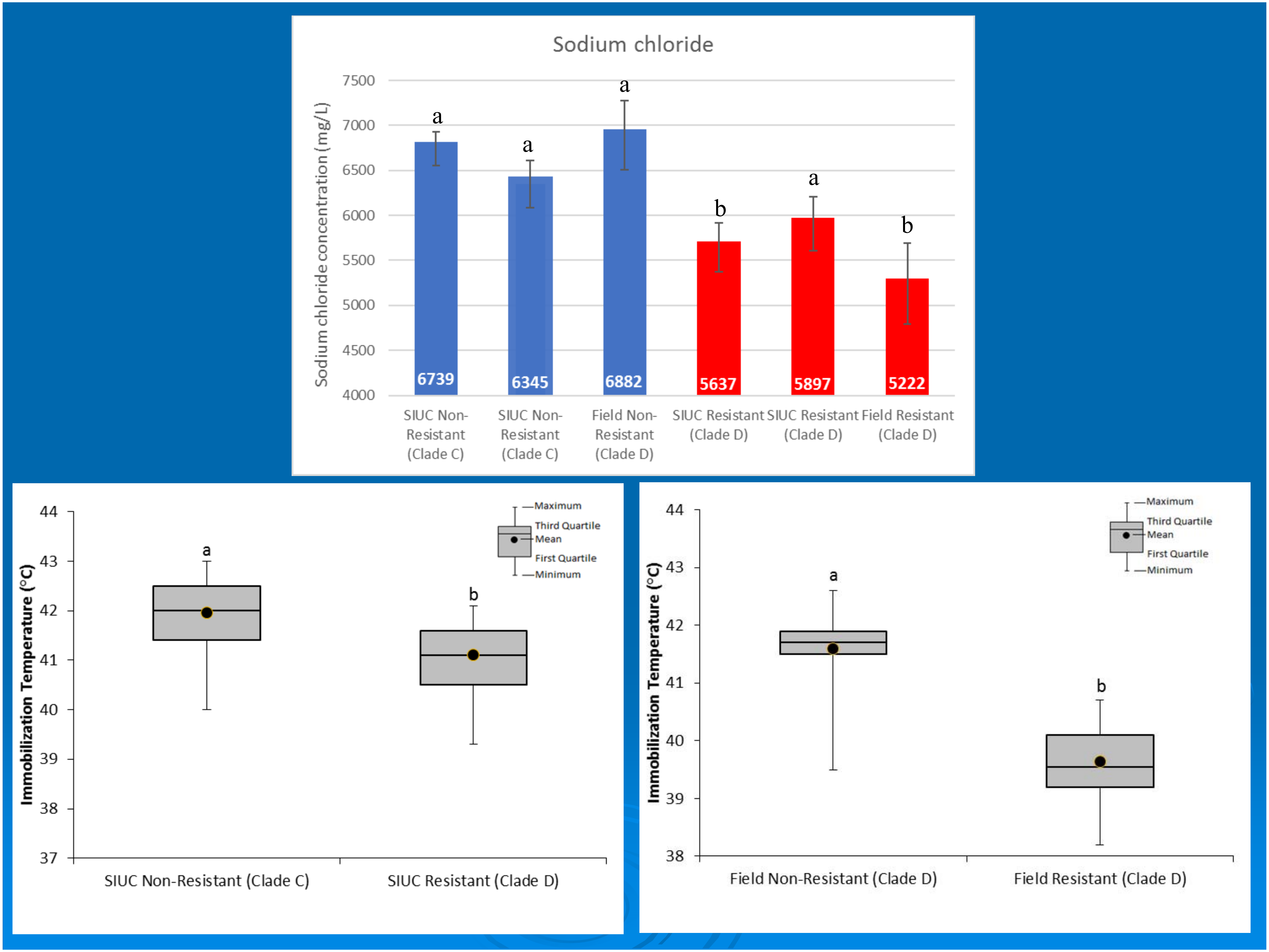
- We found detectable concentrations of permethrin and biotransformation products in fatheads fed resistant-dosed *Hyalella.*
- Transfer could be parent, biotransformation products or both.
- These body residues are most likely underestimating bioaccumulation potential at steady state.
- Exposure is expected to be even greater if other sensitive species are not able to tolerate the elevated pyrethroid exposures noted at sites…. So fish and birds are more heavily relying on resistant *Hyalella* as a food source.

Are *H. azteca* possessing the pyrethroid-resistant mutation less tolerant of other stressors?

<u>Challenges</u>:

Toxicity Tests (sodium chloride, DDT, copper sulfate)

Upper Thermal Tolerance



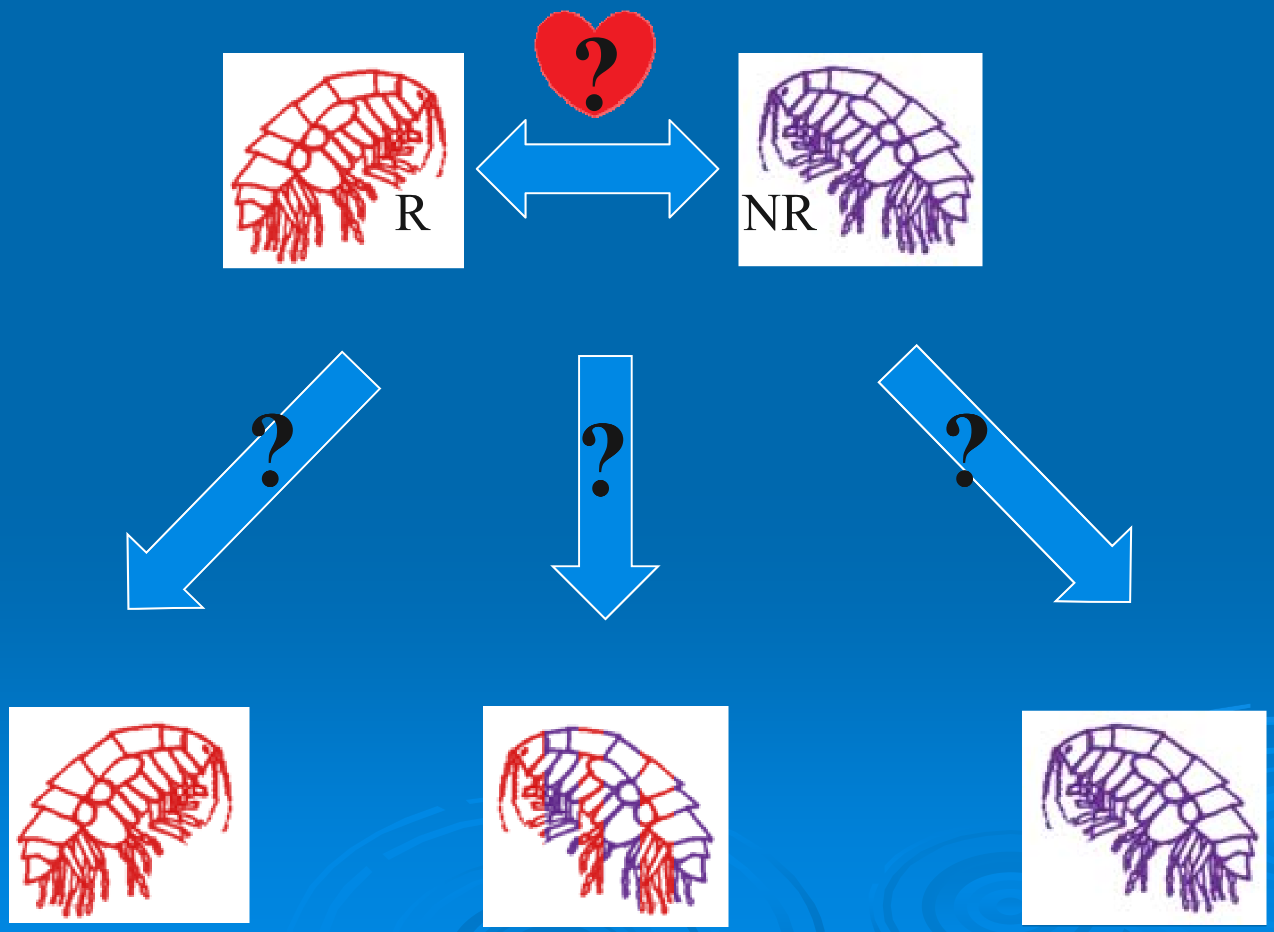
Sodium chloride
Sodium chloride concentration (mg/L)
7500
7000
6500
6000
5500
5000
4500
4000
a
a
a
b
a
b
6739
6345
6882
5637
5897
5222
SIUC Non-Resistant (Clade C)
SIUC Non-Resistant (Clade C)
Field Non-Resistant (Clade D)
SIUC Resistant (Clade D)
SIUC Resistant (Clade D)
Field Resistant (Clade D)
Immobilization Temperature (°C)
44
43
42
41
40
39
38
37
a
b
Maximum
Third Quartile
Mean
First Quartile
Minimum
SIUC Non-Resistant (Clade C)
SIUC Resistant (Clade D)
Immobilization Temperature (°C)
44
43
42
41
40
39
38
a
b
Maximum
Third Quartile
Mean
First Quartile
Minimum
Field Non-Resistant (Clade D)
Field Resistant (Clade D)

Mojave Desert

What are the “costs” of this resistance?

- Increased bioaccumulation potential
- Increased risk of biomagnification
- Decrease tolerance to other stressors
- Implications for bioassessments?

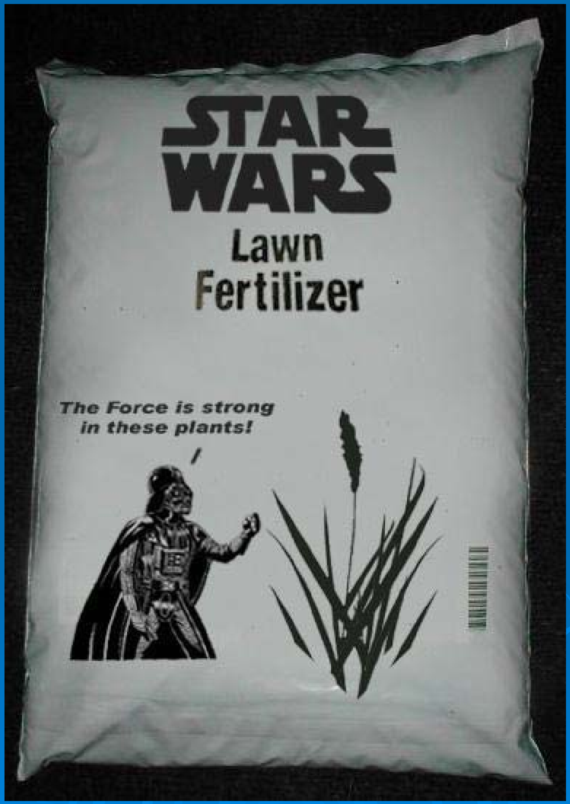
Is resistance dominant or recessive?



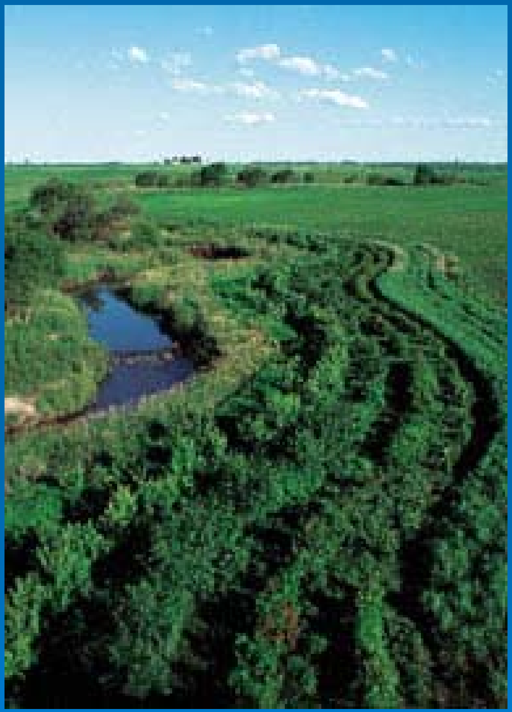
Population	Test Date	LC50 (95% Confidence Intervals)
SIUC NR	October 2015	31.22 ng/L (26.44 – 36.87) [a]
SIUC RES	October 2016	1418 ng/L (1269 - 1585) [b]
SIUC NR X SIUC RES Different clades*	October 2016	22 ng/L
Field NR X SIUC RES Same clades	February 2017	~25 ng/L

- F1 offspring are non-resistant… Mutation is recessive.

What can we do to keep pyrethroids from being an issue in urban areas?



What can we do to keep pyrethroids from being an issue in agricultural areas?



Polyacrylamide (PAM) — a commercially available, nontoxic soil stabilizer — was highly effective in reducing sediments and pyrethroids when added to irrigation water in liquid or tablet form. *Left,* untreated runoff; *right,* runoff resulting from PAM-treated irrigation source water runs clear.

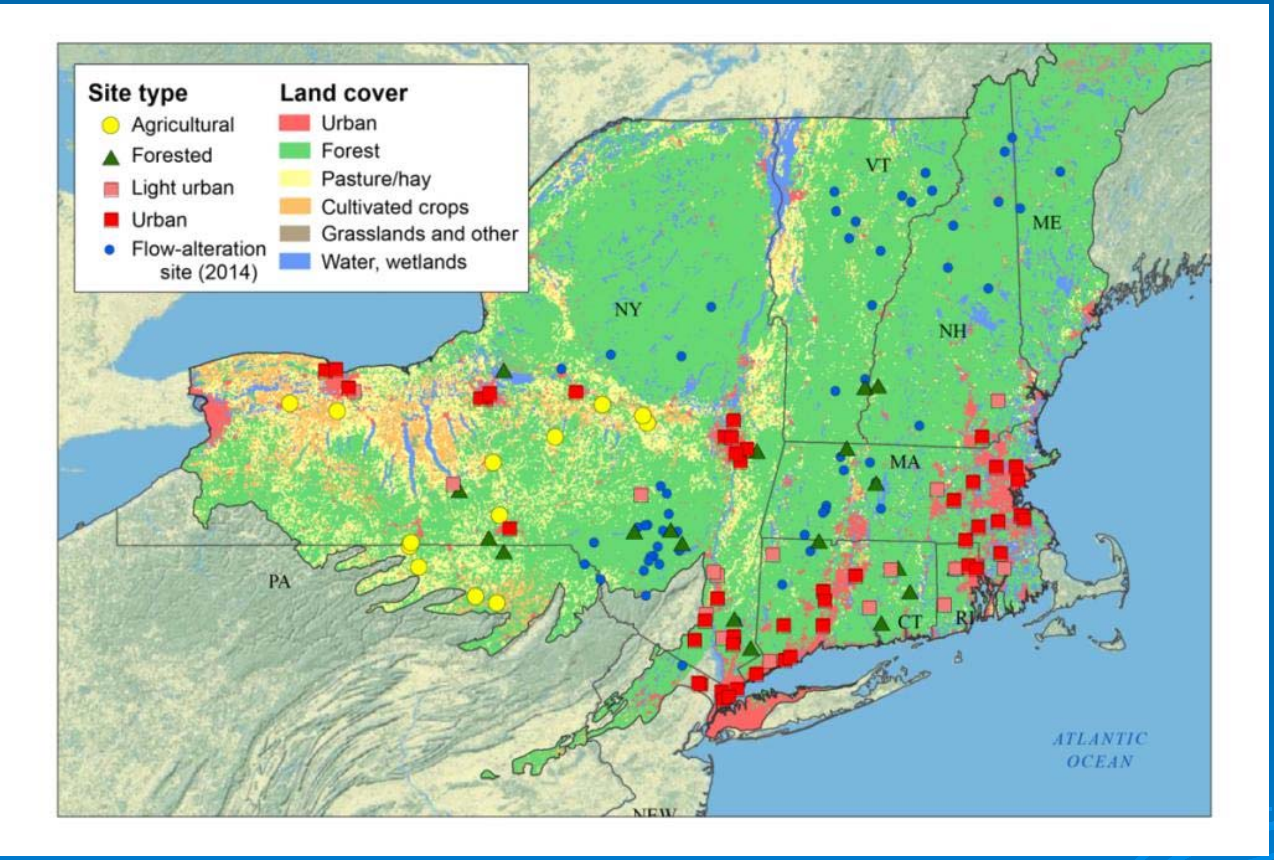
Take Home Messages

- Pyrethroids are prevalent in aquatic systems and are present at high enough concentrations to severely impact sensitive non-target species
- Elevated concentrations have been found in sediments in several countries
- Appears to be largely an urban homeowner problem
- Resistance has developed in *H. azteca* and is widespread throughout CA

Take Home Messages

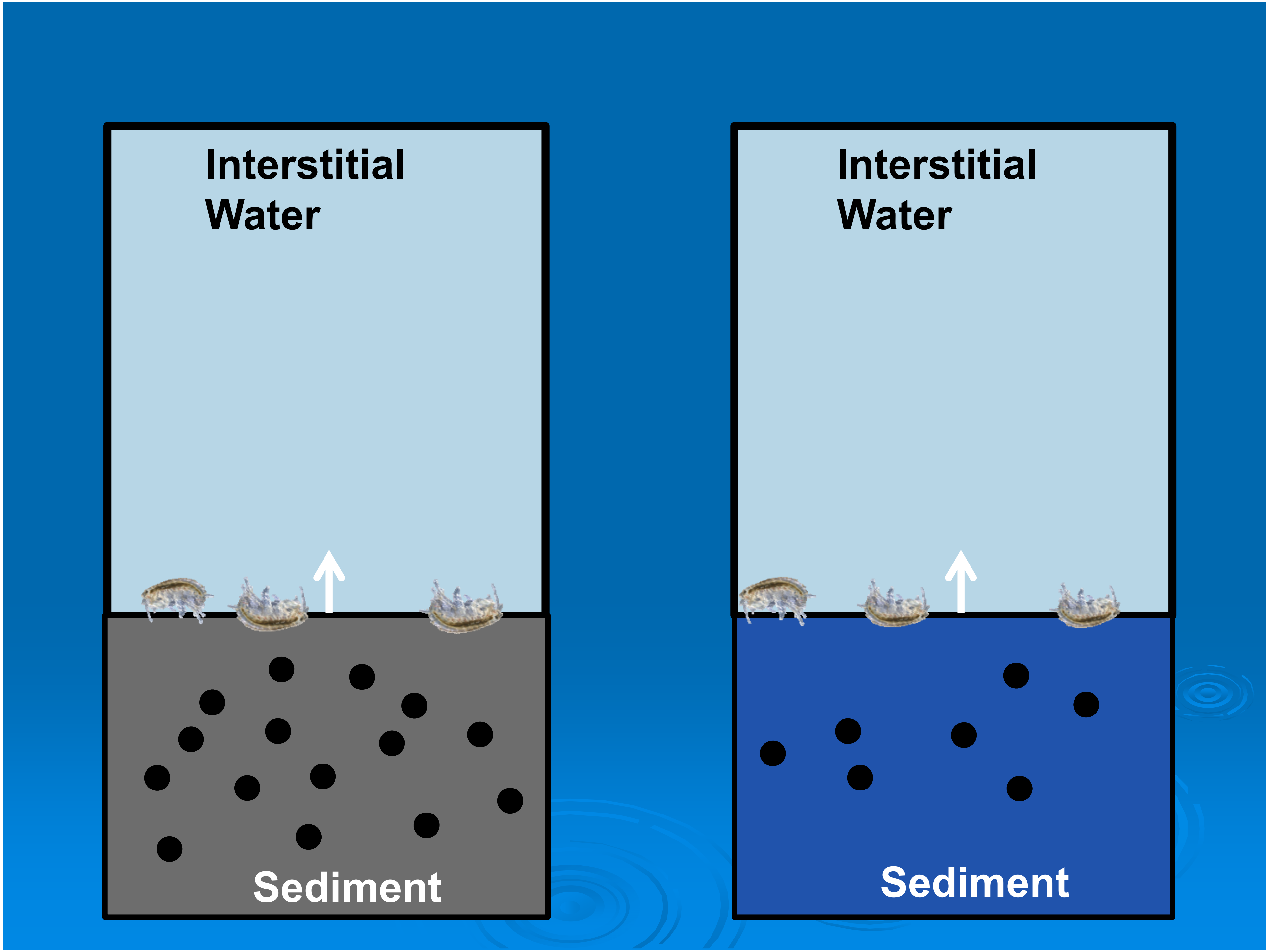
- **Adaptation** has occurred in *Hyalella* due to exposure to terrestrially-applied pyrethroids and this has been confirmed with toxicity and genetic testing.
- Non-resistant *H. azteca* cannot survive high permethrin exposure, thus pyrethroid resistance **increases the relative risk** of permethrin trophic transfer.
- Pyrethroid-resistant *H. azteca* increase fish exposure to permethrin and its biotransformation products, by adding an **additional route of exposure**.
  - Increased risk of altered sex ratios, & feminization of male fish which could result in **population declines** as estrogenic biotransformation products accumulate.

Using bioavailability to assess pyrethroid insecticide toxicity in urban sediments

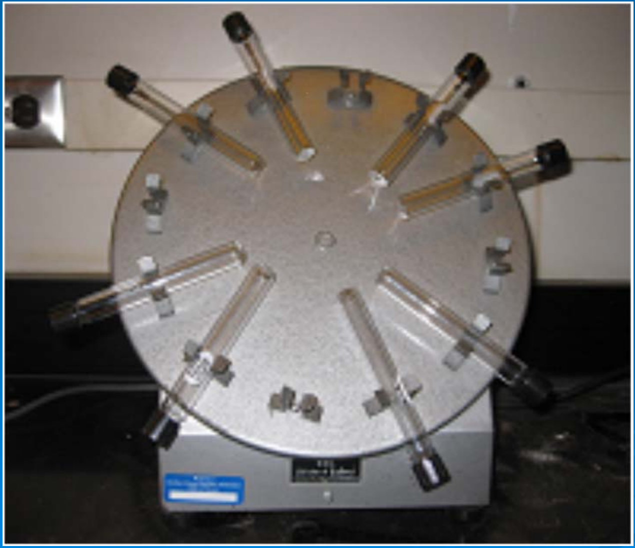


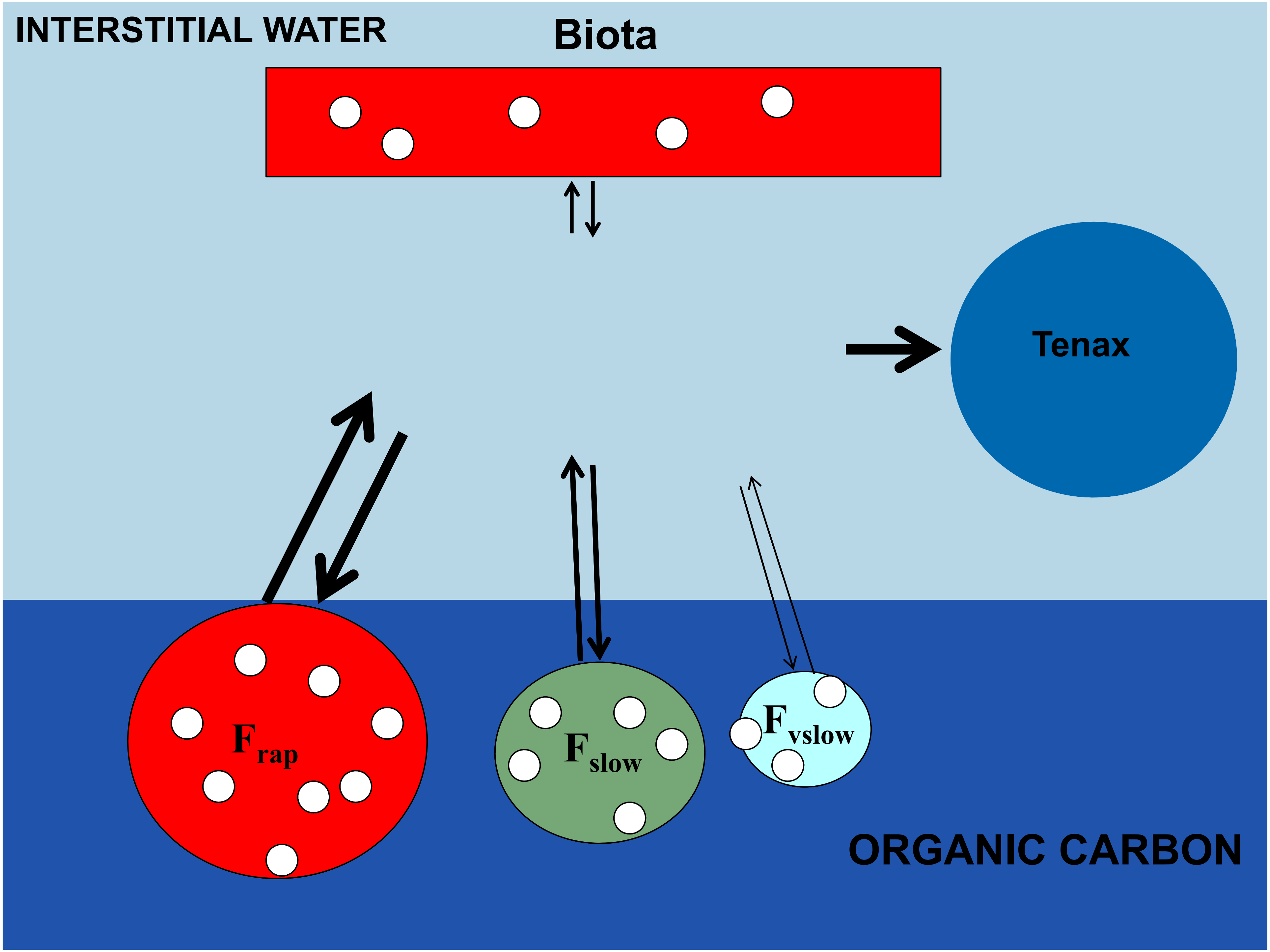
USGS 104G National Competitive Grant G15AS00019

Illinois Water Resources Center


Interstitial
Water
Sediment
Interstitial
Water
Sediment

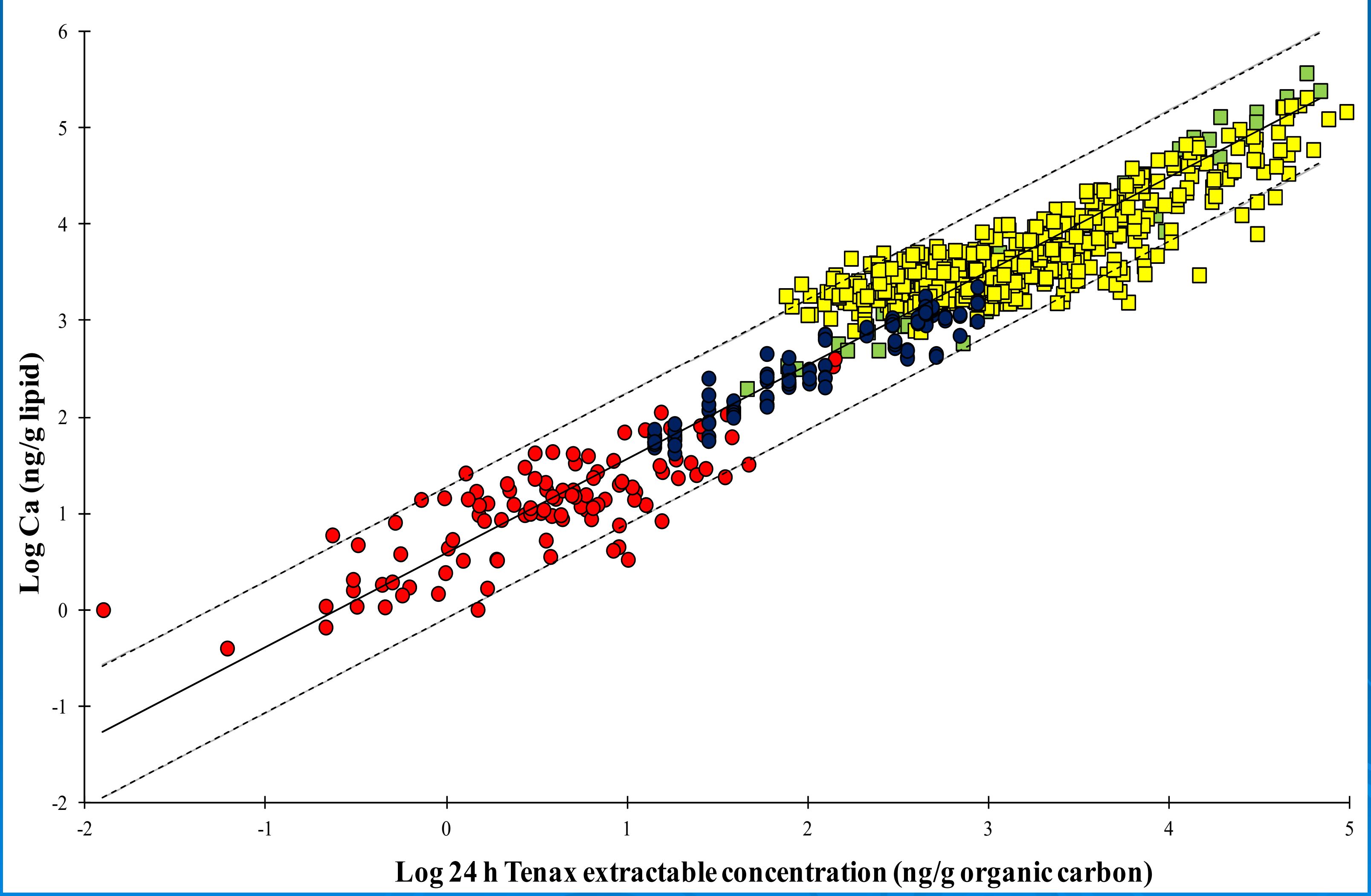
Desorption-based samplers





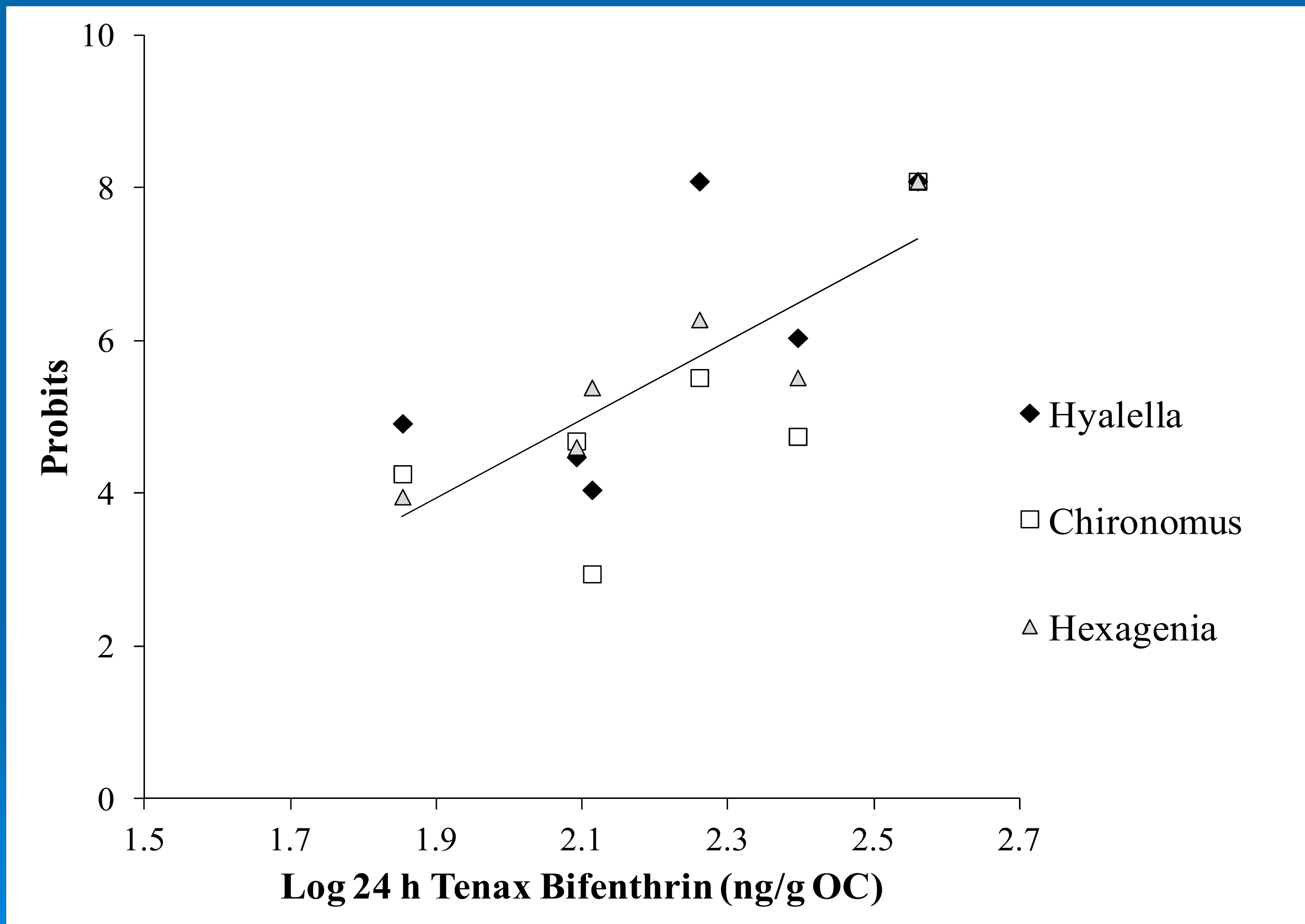
INTERSTITIAL WATER
Biota
Tenax
F_{rap}
F_{slow}
F_{vslow}
ORGANIC CARBON

Bioaccumulation Tenax Model



Harwood et al. 2015

Tenax versus Toxicity



Objectives

- Chemically analyze the sediments & run Tenax
- Toxicity bioassays

Hyalella azteca

Chironomus dilutus

Lampsilis siliquoidea

- Verify with targeted-TIEs
- Check for presence of pyrethroid-resistant *H. azteca*

Impacts of our work?

- Permissible application practices of pyrethroids by professional applicators are being modified (already done in CA).
- No longer can they spray broad areas of impervious surfaces.
- The distance up the house foundation and out from the house that they can spray are now being limited (3 feet in each direction).

Impacts of our work?

- Most pyrethroids are now being re-registered nationwide. Most of the data being used by the USEPA for this review is our data.
- In CA, our data has led to pyrethroids being placed in re-registration, a process by which the state requires registrants to produce additional data to address previously unrecognized risk.

Impacts of our work?

- Sediment toxicity testing has been added to permit requirements of stormwater agencies in Stockton and Sacramento.
- Pyrethroid monitoring and *Hyalella* testing has been added for the Sacramento POTW.
- About a dozen creeks in CA have been added to the 303(d) list due to pyrethroid impairment.

Impacts of our work?

CALIFORNIA
Water Boards

Central Valley Regional Water Quality Control Board

13 March 2015

Notice of Public Meeting
CENTRAL VALLEY PYRETHROID PESTICIDES TOTAL MAXIMUM DAILY LOAD and BASIN PLAN AMENDMENT

5 May 2015, 1 p.m.-4 p.m.
Central Valley Water Board – Training Room
(916) 574-1755

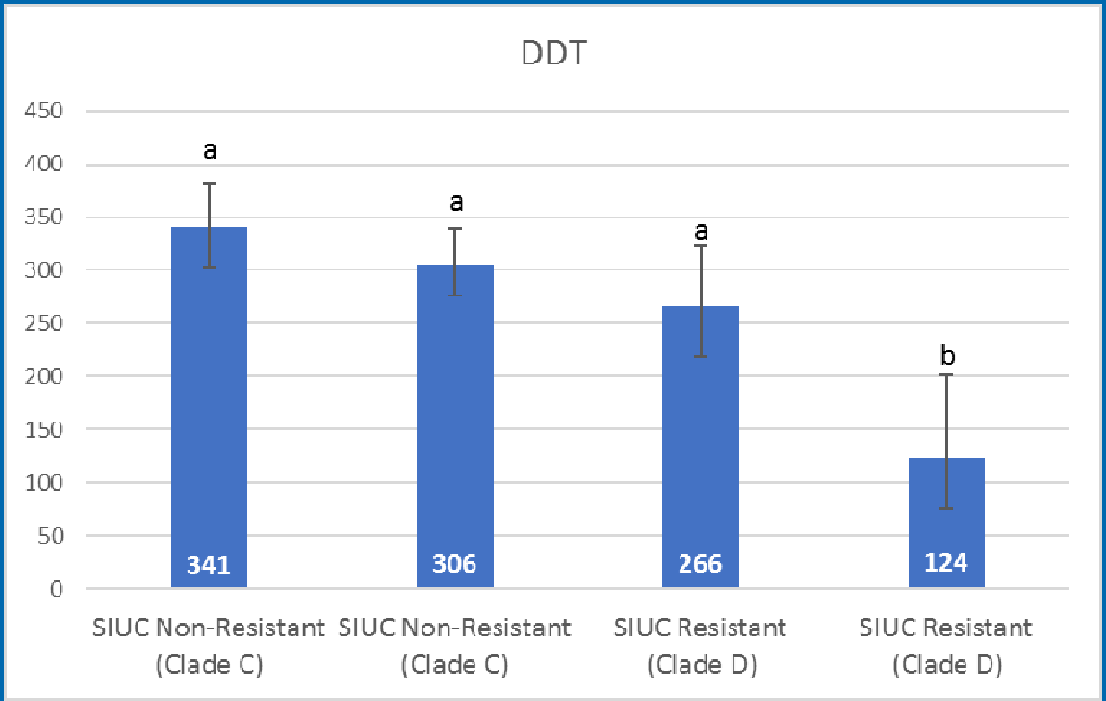
NOTICE IS HEREBY GIVEN that staff of the Central Valley Regional Water Quality Control Board (Central Valley Water Board) will hold a public meeting to discuss and provide an update

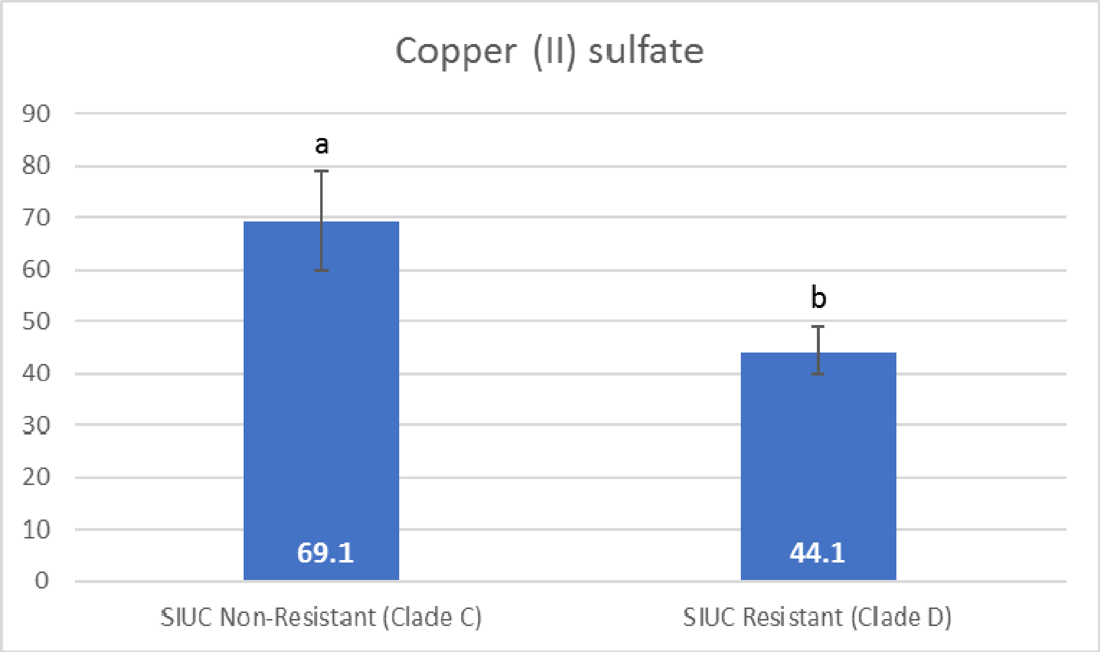
Questions ?


ENVIRONMENTAL
Science & Technology
Aquatic Toxicity Due to Residential Use of PYRETHROID INSECTICIDES
Regulating the Underground Injection of CO_2
Transgenic Plants in Phytoremediation

Impacts of pyrethroid exposure to fish

- LC_{50} values in the low µg/L range and more toxic at lower temps
- Pyrethroids effect swimming behavior and other behavioral endpoints
- DeGroot and Brander (2014) found that pyrethroid biotransformation products were the main contributors to estrogenic effects in fish
- 3-phenoxybenzyl alcohol and 3-(4′-hydroxyphenoxy)-benzyl alcohol mimic the interaction of 17-β-estradiol with estrogen receptors (Nillos et al. 2010)


DDT
450
400
350
300
250
200
150
100
50
0
a
a
a
b
341
306
266
124
SIUC Non-Resistant (Clade C)
SIUC Non-Resistant (Clade C)
SIUC Resistant (Clade D)
SIUC Resistant (Clade D)


Copper (II) sulfate
90
80
70
60
50
40
30
20
10
0
a
b
69.1
44.1
SIUC Non-Resistant (Clade C)
SIUC Resistant (Clade D)

Environmental Pollution xxx (2016) 1–8

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Do pyrethroid-resistant *Hyalella azteca* have greater bioaccumulation potential compared to non-resistant populations? Implications for bioaccumulation in fish☆

Leslie L. Muggelberg [a,1], Kara E. Huff Hartz [a], Samuel A. Nutile [a], Amanda D. Harwood [b], Jennifer R. Heim [a], Andrew P. Derby [a], Donald P. Weston [c], Michael J. Lydy [a,*]

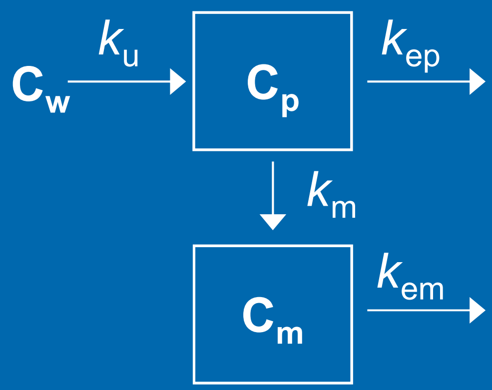
[a] *Center for Fisheries, Aquaculture and Aquatic Sciences and Department of Zoology, Southern Illinois University, Carbondale, IL 62901, USA*

[b] *Biology and Environmental Studies, Alma College, Alma, MI 48801, USA*

[c] *Department of Integrative Biology, University of California, Berkeley, CA 94720, USA*

Please cite this article in press as: Muggelberg, L.L., et al., Do pyrethroid-resistant *Hyalella azteca* have greater bioaccumulation potential compared to non-resistant populations? Implications for bioaccumulation in fish, Environmental Pollution (2016), http://dx.doi.org/10.1016/j.envpol.2016.09.073

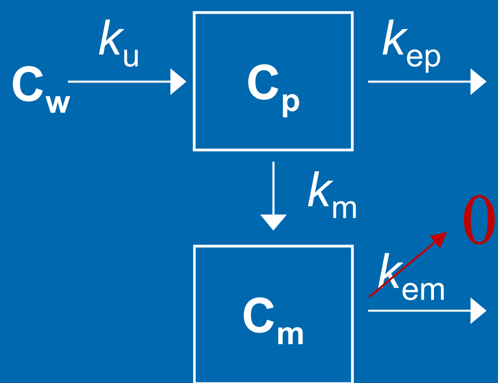
Time to Steady-State Using Toxicokinetics



$$t_{1/2} = \frac{\ln 2}{k_{ep} + k_m}$$

Two-compartment model for *H. azteca* permethrin exposure
C = concentration in water (w) or in *H. azteca* tissue
p = parent permethrin   m = permethrin biotransformation products
k= rate coefficient/ constant for u = uptake or e = elimination

Time to Steady-State Using Toxicokinetics



$$t_{1/2} = \frac{\ln 2}{k_{ep} + k_m}$$

Population	5 $t_{1/2}$
Resistant *H. azteca*	17.4 h
Non-resistant *H. azteca*	33.2 h

Two-compartment model for *H. azteca* permethrin exposure
C = concentration in water (w) or in *H. azteca* tissue
p = parent permethrin m = permethrin biotransformation products
k= rate coefficient/ constant for u = uptake or e = elimination